

Study on novel functional activated carbon and composites for adsorption heat pump systems

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Study on novel functional activated carbon and composites for adsorption heat pump systems

Dissertation

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Study on novel functional activated carbon and composites for adsorption heat pump systems

A dissertation submitted in partial fulfilment of the requirements for
the award of the degree of

Doctor of Philosophy

By

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June 2018

Dedicated to

My Parents

&

Wife

Summary

Conventional heat pump systems are responsible for the carbon footprints from the usage of considerable amount of electricity and chemical refrigerants having ODP and high GWP. Owing to the energy crisis and imposing of international regulations on the production and use of environmentally harmful refrigerants, research on adsorption heat pump (AHP) systems have been greatly intensified worldwide. Adsorption heat pump (AHP) systems being driven by industrial waste heat or solar heat offer as a promising alternative to tackle the energy crisis and environmental issues. However, their widespread adoption is hindered by advancements in the adsorbent material.

Among the various adsorbents studied so far, activated carbon (AC) has been proven potential adsorbents for AHP applications due to its high surface area and pore volume. It is also proven that adsorption uptake of ethanol and CO₂ onto AC increases with the increase of pore volume. However, the pore volume of AC found in open literature is not promising to increase the adsorption uptake at the preferred level for its commercial dissemination. Furthermore, thermal conductivity of AC is relatively poor because of its powder form and low packing density. As a result, AHP systems are bulky and low performance, which hinders for spreading this novel technology.

From the above perspective, this thesis emphasizes towards the development of high performance ACs from relatively cheap and renewable precursors and consolidated AC composite adsorbents. The research strongly stresses on two factors, firstly, on the synthesis and characterization of the highly porous ACs from the two precursor biomasses (waste palm trunk and mangrove). Secondly, it includes the synthesis and characterization of composite adsorbents to enhance the thermal conductivity into the adsorbent material. Finally, this thesis presents the feasibility study of newly developed promising biomass-derived ACs and composites from the viewpoint of AHPs application using ethanol and CO₂ as the refrigerants. Apart from the synthesis, characterization, and adsorption characteristics of ethanol and CO₂ onto biomass-derived ACs and AC composites, the thesis provides the equilibrium thermodynamic analysis of adsorbents/ethanol and adsorbents/CO₂ pairs for adsorption cooling applications.

Three types of adsorbents are synthesized; i) waste biomass-derived activated carbons (ACs), ii) AC composite adsorbents using expanded graphite (EG) and graphene

nanoplatelets (GNPs), and iii) AC composite using polymerized ionic liquid (PIL) as a binder. Experimental investigations on the surface characteristics including surface area, pore volume, and pore size distribution of all synthesized adsorbents have been furnished. The thermal diffusivity and conductivity of all developed adsorbents are measured and promising are selected for the measurement of adsorption characteristics. Surface morphology of studied biomass-derived ACs is also presented. Finally, the porous properties and thermal conductivity data are compared with the hitherto commercial adsorbent Maxsorb III.

Ethanol and CO₂ adsorption characteristics of biomass-derived ACs and AC composites have been carried out using a gravimetric method at adsorption temperatures ranging from 20 to 70°C and pressures ranges corresponding to the working conditions of adsorption cooling cycle. The experimental data are modeled for CO₂ and ethanol vapor adsorption isotherm and kinetics for the comparison. The adsorption models' parameters are optimized and accordingly their sensitivity is discussed. A comparative study between the synthesized AC based adsorbents and other ACs are also presented. It is found that the biomass-derived ACs are excellent potential adsorbent than that of any other ACs so far. A theoretical analysis of an equilibrium adsorption cooling cycle employing the biomass-derived ACs and composite adsorbents/refrigerant (ethanol and CO₂) pairs is presented using a time-independent model. The comparisons of specific cooling effect and coefficient of performances under various desorption and evaporation temperatures have been presented. The calculated SCE for ethanol and CO₂ is compared with Maxsorb III.

The pore volume of biomass-derived ACs surpasses all other ACs hitherto, which makes the benchmark. It possesses the highest pore volume is 2.87 cm³ g⁻¹ whereas Maxsorb III has only 1.70 cm³ g⁻¹. WPT-AC can adsorb up to 1.9 kg ethanol vapor per kg of adsorbent and shows 35% higher than net uptake of Maxsorb III/ethanol. Furthermore, WPT-AC (WC500)/CO₂ pair shows the adsorption uptake 2.6 cm³ g⁻¹, which is also 73% improvement compared to Maxsorb III/CO₂. It is the current benchmark. Expanded graphite (EG) contained AC composite possesses 11 times whilst GNPs contained AC composite shows 23.5 higher thermal conductivity than parent AC. Polymerized ionic liquid (PIL) binder based composite has 11% and 18% higher surface area and pore volume than that of any other conventional synthetic binders based composites. WPT-AC/ethanol adsorption cycle shows 36% higher SCE whilst M-AC/ethanol pair gives about 32% higher SCE compared to Maxsorb III/ethanol. In addition, biomass-derived ACs/CO₂ pair provides about 55 to 92% higher SCE compared to Maxsorb III/CO₂.

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List of Publications

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Journal papers:

1. **A. Pal**, A. Kondor, S. Mitra, K. Thu, B.B. Saha, On surface energy and acid-base properties of highly porous parent and surface treated activated carbons using inverse gas chromatography, J. Ind. Eng. Chem., Accepted (July 2018).
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3. **A. Pal**, M.S.R. Shahrom, M. Moniruzzaman, C.D. Wilfred, S. Mitra, K. Thu, B.B. Saha, Ionic liquid as a new binder for activated carbon based consolidated composite adsorbents, Chem. Eng. J. 326 (2017) 980-986.
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1. **A. Pal***, K. Thu, B.B. Saha, Effect of adsorbent layer height on instantaneous adsorption capacity, *Proceedings of International Forum for Green Asia 2017*, pp. 26-29, Fukuoka, Japan, Nov. 29, 2017
2. **A. Pal***, S. Mitra, K. Thu, B.B. Saha, Improved adsorption uptake of ethanol and CO₂ onto biomass based activated carbons, *Proceedings of 3rd International Exchange and Innovation Conference on Engineering & Sciences (IEICES2017)*, pp. 127-128, Fukuoka, Japan, Oct. 19-20, 2017. Presentation style: Oral.
3. **A. Pal***, S. Mitra, K. Thu, B.B. Saha, Enhanced CO₂ adsorption onto biomass based activated carbon, *Proceedings of International Sorption Heat Pump Conference 2017 (ISHPC2017)*, Paper No. AD-YR1-1147, Tokyo, Japan, Aug. 7-10, 2017. Presentation style: Oral.
4. M. M. Younes, I.I. El-Sharkawy, A.E. Kabeel, **A. Pal***, K. Thu, B.B. Saha, Thermo-Physical Properties of Silica Gel Composites for Adsorption Cooling and Desalination Applications, *Proceedings of International Sorption Heat Pump Conference 2017 (ISHPC2017)*, Paper No. AD-MA-1141, Tokyo, Japan, Aug. 7-10, 2017. Presentation style: Oral.
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6. S. Mitra*, **A. Pal**, K. Thu, B.B. Saha, Transient numerical study of novel composite adsorbent for cooling applications, Thermal and Fluid Engineering Conference (TFEC2017), pp. 37-46, Las Vegas, USA, Apr. 2-5, 2017. Presentation style: Oral.
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8. S. Mitra*, **A. Pal**, B.B. Saha, “Thermally driven adsorption system for sustainable energy technology”, JSPS-DST Asian Academic Seminar, Dec. 14–20, 2016 Tokyo, Japan. Presentation style: Poster.
9. M.T. Kibria*, **A. Pal**, T. Nakagawa, S. Mizuno, B.B. Saha, Effect of binders onto adsorption characterization of activated carbon based composites, Proceedings of 18th CSS-EEST, Shanghai, China, Dec. 4-6, 2016. Presentation style: Poster
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12. H.-S. Kil, **A. Pal**, B.B. Saha, I. Mochida, K. Nakabayashi, S.-H. Yoon, J. Miyawaki*, Preparation and ethanol adsorption properties of activated carbons from biomass for adsorption heat pumps, Proceedings of IVth International Symposium on Innovative Materials for Processes in Energy System (IMPRES2016), pp. 289-290, Italy, Oct. 23-26, 2016. Presentation style: Oral.
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14. **A. Pal***, I.I. El-Sharkawy, B.B. Saha, T. Miyazaki, S. Koyama, Preparation and characterization of consolidated composite adsorbents for cooling application,

Proceedings of 53rd National Heat Transfer Symposium, Japan, May 24-26 2016.
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Table of Contents

Summary.....	i
Acknowledgements	iii
List of Publications	v
Table of Contents	ix
List of Figures.....	xiv
List of Tables	xxii
Nomenclature	xxiv
Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Historical development of refrigerants	3
1.3 GWP and ODP of commonly used refrigerants.....	4
1.4 Assessment of global warming potential	6
1.5 Motivation	10
1.6 Aims and objectives of the thesis	11
1.7 Organization of the thesis.....	12
Chapter 2 Literature review	15
2.1 Adsorption cooling system	15
2.1.1 Adsorption process	15
2.1.2 Working principle of adsorption cooling systems.....	17
2.1.3 Adsorbent	19
2.1.4 Adsorbate	22
2.2 Fundamental characterization	23
2.2.1 Porous properties.....	23
2.2.2 Uptake and kinetics measurement techniques.....	24
2.2.3 Adsorption isotherms and kinetics	25
2.2.4 Thermal properties	26
2.2.4.1 Thermal conductivity of ACs.....	26

2.2.4.2	Isosteric heat of adsorption	27
2.2.4.3	Specific heat capacity of ACs	29
2.3	Activated carbon based adsorption cooling systems	30
2.3.1	Activated carbon/ethanol pair	30
2.3.2	Activated carbon/methanol pair	31
2.3.3	Activated carbon/carbon dioxide (CO ₂) pair	32
2.3.4	AC based consolidated composites	33
2.4	Scope of this thesis	35
2.5	Approaches to this thesis	37
2.5.1	Effective uptake improvement approach	38
2.5.2	Thermal conductivity improvement approach	39
Chapter 3	Development of adsorbent material	41
3.1	Introduction	41
3.2	Synthesis and characterization biomass-derived functional ACs	43
3.2.1	Precursor materials	44
3.2.2	Experiments	45
3.2.2.1	Carbonization	45
3.2.2.2	Activation	49
3.2.3	Characteristics of synthesized AC samples	51
3.2.3.1	Porous properties	52
3.2.3.2	Scanning electron microscopy (SEM) observation	58
3.2.3.3	Thermal conductivity of biomass-derived ACs	60
3.2.3.4	Choice of optimal AC	61
3.3	Synthesis and characterization of AC based composite adsorbents	62
3.3.1	Materials	62
3.3.1.1	Activated carbon (Maxsorb III)	62
3.3.1.2	Expanded graphite (EG)	63
3.3.1.3	Graphene nanoplatelets (GNPs)	64
3.3.1.4	Polyvinyl alcohol (PVA)	65
3.3.2	Composite adsorbents using EG as a thermal conductivity enhancer	66
3.3.3	Composite adsorbents using GNPs as a thermal conductivity enhancer	68
3.3.4	Experiments	69
3.3.4.1	N ₂ adsorption	69

3.3.4.2 Thermal diffusivity and conductivity measurement of composites	70
3.3.5 Characteristics of synthesized composites	73
3.3.5.1 EG contained composites.....	73
3.3.5.2 GNPs contained composites	78
3.3.6 Polymerized amino acid based ionic liquid (PAAIL) as a binder	86
3.3.6.1 Chemicals.....	86
3.3.6.2 Synthesis of PAAIL	86
3.3.6.3 Characteristics of polymerized AAIL (PAAIL)	87
3.3.6.4 Poly IL [VBTMA][Ala] as a binder for AC composite.....	90
3.3.6.5 Characteristics of composites	92
3.4 Conclusions.....	96
Chapter 4 Application to low pressure adsorption systems.....	99
4.1 Introduction.....	99
4.2 Experiment for adsorption characteristics	100
4.2.1 Test rig for adsorption uptake measurement	100
4.2.2 Gravimetrically adsorption uptake measurement.....	102
4.3 Theory of adsorption isotherm and kinetics models	104
4.3.1 Adsorption isotherms	104
4.3.2 Adsorption kinetics.....	105
4.4 Biomass-derived AC/ethanol pairs	106
4.4.1 Adsorption isotherm	106
4.4.2 Adsorption kinetics.....	109
4.5 Composites/ethanol pairs.....	119
4.5.1 EG contained composites/ethanol pairs	119
4.5.1.1 Adsorption isotherms	119
4.5.2 GNPs contained composites/ethanol pairs	123
4.5.2.1 Adsorption isotherms	123
4.5.2.2 Adsorption kinetics	127
4.5.3 PAAIL binder based composite	129
4.5.3.1 Adsorption isotherms	129
4.6 Conclusions.....	133

Chapter 5 Application to high pressure adsorption systems	136
5.1 Introduction.....	136
5.2 Experiment of adsorption characteristics.....	137
5.2.1 Instrumentation.....	137
5.2.2 Procedure.....	138
5.3 Theory of adsorption isotherm models	139
5.4 Excess and absolute adsorption	141
5.5 Biomass-derived ACs/CO ₂ pairs	141
5.5.1 Adsorption isotherm.....	141
5.5.2 Adsorption kinetics.....	150
5.6 Composites/CO ₂ pairs.....	152
5.6.1 EG contained composites/CO ₂ pairs	152
5.6.2 GNPs contained composites/CO ₂ pairs	156
5.6.2.1 Adsorption isotherms	156
5.6.2.2 Adsorption kinetics	159
5.7 Conclusions.....	161
Chapter 6 Thermodynamic analysis of an adsorption cooling cycle.....	163
6.1 Introduction.....	163
6.2 Thermodynamic cycle.....	164
6.3 Effect of operating temperature on SCE and COP	169
6.3.1 Ethanol as a refrigerant.....	169
6.3.1.1 Biomass-derived ACs	169
6.3.1.2 Composite adsorbents	174
6.3.2 CO ₂ as a refrigerant	178
6.3.2.1 Biomass-derived ACs	178
6.3.2.2 Composite adsorbents	181
6.4 Comparison of thermodynamic parameters	183
6.5 Conclusions.....	184
Chapter 7 Overall conclusions and recommendations	185
7.1 Overall conclusions.....	185
7.2 Recommendations.....	191
References.....	192

Appendix A. Uncertainty analysis	210
Appendix B. Surface characterization analyzer (3Flex™)	212
Appendix C. Thermal diffusivity analyzer (LFA457)-laser flash method.....	215
Appendix D. C-Therm TCi thermal conductivity analyzer- modified transient plane source method.....	219
Appendix E. Experimental uptake of WPT-AC/ethanol.....	221
Appendix F. Experimental uptake of composite C/CO₂	223

List of Figures

Fig. 1.1	Schematic diagram of a conventional heat pump system.	3
Fig. 1.2	Refrigerant progression [19].	4
Fig. 1.3	Specific charge amount in complete systems for different applications using different refrigerants [24].	8
Fig. 1.4	Direct emission amount of CO ₂ per kW/year from the residential air-conditioner.	9
Fig. 1.5	Comparison of direct emission amount of CO ₂ per kW/year from the various system.	9
Fig. 2.1	a) Schematic of adsorption process b) Adsorption isotherms.	16
Fig. 2.2	Schematic diagram of basic adsorption cooling system.	17
Fig. 2.3	Thermodynamic cycle (P-T-W diagram) of a basic adsorption cooling system.	19
Fig. 2.4	Equilibrium ethanol and CO ₂ adsorption uptake onto various activated carbon based adsorbent as a function of pore volume [14–16,18,36,37,39,52].	24
Fig. 2.5	Manufacture processes of consolidated composite AC.	34
Fig. 2.6	Consolidated composite adsorbents, (a) density of 249 kgm ⁻³ with cracks, (b) density of 388 kgm ⁻³ without cracks, (c) density of 448 kgm ⁻³ with cracks [69].	35
Fig. 2.7	Parameters affect the system performance and compactness.	38
Fig. 2.8	Schematic representation of effective uptake definition and way to obtain large pore volume with high surface area ACs.	39
Fig. 2.9	Schematic drawing of creating thermal network using additives.	40
Fig. 3.1	Pictorial view of two raw biomasses employed for synthesis of functional ACs.	45
Fig. 3.2	Crushing and drying (a) WPT and (b) Mangrove.	46
Fig. 3.3	Processing steps for preparation of biomass-derived activated carbons [113].	47
Fig. 3.4	Schematic diagram of experimental setup for carbonization and KOH activation reactor.	48
Fig. 3.5	Photograph of carbonized (a) WPT and (b) Mangrove.	48

Fig. 3.6	N ₂ adsorption/desorption isotherms of WPT-derived ACs at 77 K.	53
Fig. 3.7	N ₂ adsorption/desorption isotherms of M-derived ACs at 77 K.	53
Fig. 3.8	Pore size distribution of WPT-derived ACs.	54
Fig. 3.9	Pore size distribution of M-derived ACs.	55
Fig. 3.10	Influence of activation temperature on surface area.	57
Fig. 3.11	Influence of activation temperature on pore volume.	57
Fig. 3.12	Influence of activation temperature on average pore width.	58
Fig. 3.13	SEM images of WPT-derived ACs (a) WC500A600K4; (b) WC500A700K4; (c) WC500A800K4; (d) WC500A700K6; (e) WC500A900K6, and (f) WC600A700K6	59
Fig. 3.14	SEM images of mangrove-derived ACs (a) MC500A600K4; (b) MC500A700K4; (c) MC500A800K4; (d) MC500A700K6; (e) MC500A900K6, and (f) MC600A700K6.	59
Fig. 3.15	Thermal conductivity results of all WPT-derived ACs.	60
Fig. 3.16	Thermal conductivity results of all M-derived ACs.	61
Fig. 3.17	SEM photograph of activated carbon powder (Maxsorb III) [15]	62
Fig. 3.18	SEM photograph of EG (EC500).	64
Fig. 3.19	SEM photograph of GNPs; (a) H25 and (b) C750 [127].	65
Fig. 3.20	Photograph of Polyvinyl alcohol (PVA).	66
Fig. 3.21	(a) Production process of synthesized composite adsorbents, (b) a pictorial view of synthesized composite adsorbents.	67
Fig. 3.22	Synthesis procedure and pictorial view of synthesized GNPs contained composites.	68
Fig. 3.23	Schematic diagram of 3Flex™ Surface Characterization Analyzer.	69
Fig. 3.24	Schematic design of LFA 457 MicroFlash system.	71
Fig. 3.25	An illustration of detector signal with a fitted model for GNPs contained composite 2 and composite 4.	72
Fig. 3.26	Nitrogen adsorption/desorption isotherm onto various composites.	74
Fig. 3.27	The pore size distribution of various consolidated composite samples.	75
Fig. 3.28	Plots of thermal diffusivity versus the percentage of expanded graphite.	76
Fig. 3.29	Plots of thermal conductivity versus the percentage of expanded graphite.	77
Fig. 3.30	Plots of thermal conductivity of composite A (50% Maxsorb III, 40% EG, 10% binder) versus the packing density.	77

Fig. 3.31	N ₂ gas adsorption/desorption isotherm of parent and studied composite adsorbents at 77 K.....	79
Fig. 3.32	The pore size distribution of parent Maxsorb III and composite.....	79
Fig. 3.33	Thermal diffusivity versus temperature for composite 2, 3 and 4.	81
Fig. 3.34	Thermal conductivity versus temperature for Composite_1, 2 and 3.	82
Fig. 3.35	Thermal diffusivities versus percentage of graphene (H25) content into the composite.	83
Fig. 3.36	Thermal conductivity versus percentage of graphene (H25) content into the composite.	83
Fig. 3.37	Thermal diffusivities versus packing density of composite 3.....	84
Fig. 3.38	Thermal conductivity versus packing density of composite 3.....	85
Fig. 3.39	Thermal conductivity improvement compared to Maxsorb III.....	85
Fig. 3.40	Synthesis route of polymerized AAIL (PAAIL).....	87
Fig. 3.41	Molecular structures of the monomer and polymer forms of amino acid based ionic liquid.	88
Fig. 3.42	¹ H-NMR spectrum of monomer form of [VBTMA][Ala]. The numbers below each signal are the integral values and are used to quantify the <i>proton</i> in [VBTMA][Ala].	89
Fig. 3.43	¹ H-NMR spectrum of polymer form of [VBTMA][Ala]. The numbers below each signal are the integral values and are used to quantify the <i>proton</i> in Poly IL [VBTMA][Ala].	90
Fig. 3.44	Schematic diagram of the composite synthesis process.....	91
Fig. 3.45	Comparison of volumetric adsorption uptake of CO ₂ onto Maxsorb III and composite with PIL as a binder at adsorption temperature 303.15 K.	92
Fig. 3.46	Comparison of N ₂ gas adsorption/desorption between Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) and Maxsorb III (90 wt%) + PVA (10 wt%) at 77 K.	93
Fig. 3.47	Pore size distribution of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) and Maxsorb III (90 wt%) + PVA (10 wt%).....	94
Fig. 3.48	Comparison of thermal conductivity of among Maxsorb III, Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%), and Maxsorb III (90 wt%) + PVA (10 wt%).....	95
Fig. 4.1	Schematic diagram of the experimental apparatus for measuring adsorption uptake of ethanol onto composite adsorbents.	102

Fig. 4.2	Schematic diagram of the experimental apparatus for measuring ethanol adsorption characteristics.....	104
Fig. 4.3	Adsorption isotherms of ethanol onto WPT-AC (WC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, Tóth model).	107
Fig. 4.4	Adsorption isotherms of ethanol onto M-AC (MC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, Tóth model).....	108
Fig. 4.5	Temporal histories of adsorption uptake and pressure of WPT-AC/ethanol pair at adsorption temperature 40°C.	110
Fig. 4.6	Temporal histories of adsorption uptake and pressure of WPT-AC/ethanol pair at adsorption temperature 70°C.	111
Fig. 4.7	Temporal histories of adsorption uptake and pressure of M-AC/ethanol pair at adsorption temperature 40°C.	111
Fig. 4.8	Temporal histories of adsorption uptake and pressure of M-AC/ethanol pair at adsorption temperature 70°C.	112
Fig. 4.9	Plot of $\ln(1 - F)$ versus time for WPT-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 2.18 kPa.	113
Fig. 4.10	Plot of $\ln(1 - F)$ versus time for M-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 5.12 kPa.	114
Fig. 4.11	Fractional uptake versus time for WPT-AC/ethanol pair at adsorption temperature 30, 50 and 70°C (symbols represent experiments and dash dot lines represent LDF model).....	114
Fig. 4.12	Fractional uptake versus time for M-AC/ethanol pair at adsorption temperature 30, 50 and 70°C (symbols represent experiments and dash dot lines represent LDF model).....	115
Fig. 4.13	Arrhenius plot of the WPT-AC/ethanol and M-AC/ethanol pairs.	117
Fig. 4.14	Comparison between adsorption uptake difference of adsorption cooling cycles using WPT-AC/ethanol (solid line) and M-AC/ethanol (dashed line) pairs at evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively.	118
Fig. 4.15	Comparison between adsorption uptake difference of adsorption cooling cycles using M-AC/ethanol (dashed line) and Maxsorb III/ethanol (solid line) [16] pairs at evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively.	118

Fig. 4.16	Adsorption isobars of ethanol onto composite A (50% Maxsorb III, 40% EG, 10% binder) with packing density of 517 kg m^{-3} (error bars of uptake is $\pm 5\%$).	120
Fig. 4.17	Adsorption isobars of ethanol onto composite C (70% Maxsorb III, 20% EG, 10% binder) with packing density of 446 kg m^{-3} (error bars of uptake is $\pm 5\%$).	121
Fig. 4.18	Predicted volumetric adsorption isotherms of composite adsorbent A (50% Maxsorb III, 40% EG, 10% binder)/ethanol pair with packing density of 517 kg m^{-3}	121
Fig. 4.19	Predicted volumetric adsorption isotherms of composite adsorbent C (70% Maxsorb III, 20% EG, 10% binder)/ethanol pair with packing density of 446 kg m^{-3}	122
Fig. 4.20	Comparison between volumetric adsorption uptake difference of adsorption cooling cycles using Maxsorb III/ethanol and composite C/ethanol pairs at the evaporator, adsorption and desorption temperatures of 7, 30 and 80°C , respectively.	122
Fig. 4.21	Experimental data of composite 1 ($\rho = 316 \text{ kg m}^{-3}$) fitted with studied isotherm models.	123
Fig. 4.22	Experimental data of composite 2 ($\rho = 399 \text{ kg m}^{-3}$) fitted with studied isotherm models.	124
Fig. 4.23	Experimental data of composite 3 ($\rho = 498 \text{ kg m}^{-3}$) fitted with studied isotherm models.	124
Fig. 4.24	Experimental data of composite 4 ($\rho = 388 \text{ kg m}^{-3}$) fitted with studied isotherm models.	125
Fig. 4.25	Improvement of effective volumetric (kg m^{-3}) adsorption uptake compares to parent adsorbent (Maxsorb III) at evaporator, adsorption and desorption temperatures of 15, 30 and 85°C , respectively.	127
Fig. 4.26	Dynamic adsorption uptake of all studied adsorbents (a) normalized; (b) absolute at adsorption temperature 30°C and evaporator pressure 1.8 kPa.	129
Fig. 4.27	Equilibrium adsorption uptake of ethanol onto composite A: Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) (fitted with D-A equation).	130

Fig. 4.28	Temporal histories of adsorption uptake and pressure of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol pair at adsorption temperature 323.15 K.....	131
Fig. 4.29	Volumetric adsorption uptake of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol pair at adsorption temperature ranging from 303.15 K to 353.15 K.....	132
Fig. 4.30	Comparison of adsorption uptake difference of adsorption cooling cycle between composite A: Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol (solid line) and Maxsorb/ethanol (dashed line) pairs at evaporator, adsorption and desorption temperatures of 280.15, 303.15 and 353.15 K, respectively.	133
Fig. 5.1	Schematic diagram of the experimental apparatus for measuring CO ₂ adsorption characteristics.....	139
Fig. 5.2	Adsorption isotherms of WC500 (WC500A900K6/CO ₂ pair (data are fitted with (a) Tóth and (b) modified D-A model).	143
Fig. 5.3	Adsorption isotherms of WC600 (WC600A900K6)/CO ₂ (data are fitted with (a) Tóth and (b) modified D-A model).	144
Fig. 5.4	Adsorption isotherms of MC500 (MC500A900K6/CO ₂ pair (data are fitted with (a) Tóth and (b) modified D-A model).	145
Fig. 5.5	Adsorption isotherms of MC600 (MC600A900K6)/CO ₂ (data are fitted with (a) Tóth and (b) modified D-A model).	146
Fig. 5.6	Effective uptake (ΔW) as a function of adsorbent pore volume.	149
Fig. 5.7	ΔW improvement of biomass-derived ACs with the comparison of Maxsorb III and Norit RB3 at evaporation, adsorption, and desorption temperature are 15, 28 and 85°C.....	150
Fig. 5.8	Normalized adsorption uptake as a function of time for all biomass-derived ACs/CO ₂ pairs along with Maxsorb III/CO ₂ pair at adsorption temperature 30°C and evaporator pressure about 560 kPa.	151
Fig. 5.9	Instantaneous absolute uptake of all biomass-derived ACs/CO ₂ pairs along with Maxsorb III/CO ₂ pair at same condition presented in Fig. 5.8.	151
Fig. 5.10	Adsorption isotherms of CO ₂ onto composite C (data are fitted with Langmuir model).	153

Fig. 5.11	Adsorption isotherms of CO ₂ onto composite C (data are fitted with modified Dubinin-Astakhov (D-A) equation).	153
Fig. 5.12	Adsorption isotherms of CO ₂ onto composite C (data are fitted with Tóth model).	154
Fig. 5.13	Characteristic curve for the composite C/CO ₂ pair using modified Dubinin-Astakhov (D-A) equation.	155
Fig. 5.14	Comparison of volumetric adsorption uptake of CO ₂ among studied consolidated composite, Saha et al. [52] and Himeno et al. [36].	155
Fig. 5.15	Adsorption isotherms of the composite 1/CO ₂ pair (data are fitted with Tóth and modified D-A model).	157
Fig. 5.16	Adsorption isotherms of the composite 2/CO ₂ pair (data are fitted with Tóth and modified D-A model).	157
Fig. 5.17	Adsorption isotherms of the composite 4/CO ₂ pair (data are fitted with Tóth and modified D-A model).	158
Fig. 5.18	Normalized adsorption uptake as a function of time for all composites/CO ₂ pairs along with Maxsorb III/CO ₂ pair at adsorption temperature 30°C and evaporator pressure about 560 kPa.	160
Fig. 5.19	Instantaneous absolute uptake of all composites/CO ₂ pairs along with Maxsorb III/CO ₂ pair at same condition presented in Fig. 5.18.	160
Fig. 6.1	Schematic diagram of basic adsorption cooling system.	165
Fig. 6.2	Thermodynamic process of the basic adsorption cooling cycle.	166
Fig. 6.3	A representative illustration of P-T-W diagram with adsorption cycle of (a) composite A (50% Maxsorb III + 40% EG + 10% PVA)/ethanol pair, and (b) composite C (50% Maxsorb III + 40% EG + 10% PVA)/ethanol pair.	167
Fig. 6.4	Specific cooling effect (SCE) of WPT-AC (WC600A900K6)/ethanol pair with a function of desorption temperature.	170
Fig. 6.5	Specific cooling effect (SCE) of M-AC (MC600A900K6)/ethanol pair with a function of desorption temperature.	171
Fig. 6.6	Comparison of specific cooling effect (SCE) among biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.	171
Fig. 6.7	COP of WPT-AC (WC600A900K6)/ethanol with a function of desorption temperature.	173

Fig. 6.8	COP of M-AC (MC600A900K6)/ethanol with a function of desorption temperature.....	173
Fig. 6.9	Comparison of COP among biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.....	174
Fig. 6.10	A representative illustration of SCE of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair with a function of desorption temperature.....	175
Fig. 6.11	Comparison of specific cooling effect (SCE) among all studied composites/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.....	176
Fig. 6.12	A representative illustration of COP of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair with the function of desorption temperature.....	177
Fig. 6.13	Comparison of COP among all studied composites/ethanol pairs at evaporator temperature 15°C and adsorption temperature 30°C with the function of desorption temperature.....	177
Fig. 6.14	Specific cooling effect (SCE) of WPT-AC (WC500A900K6)/CO ₂ pair with a function of desorption temperature.	178
Fig. 6.15	Specific cooling effect (SCE) of M-AC (MC500A900K6)/CO ₂ with a function of desorption temperature.	179
Fig. 6.16	Comparison of specific cooling effect (SCE) among biomass-derived ACs/CO ₂ and Maxsorb III/CO ₂ pair at evaporator temperature 15°C with function of desorption temperature.	180
Fig. 6.17	Comparison of COP among biomass-derived ACs and Maxsorb III at evaporator temperature 15°C with function of desorption temperature.	181
Fig. 6.18	A representative illustration of SCE of composite 1(90 wt% Maxsorb III + 10 wt% PVA)/CO ₂ pair with the function of desorption temperature.	182
Fig. 6.19	Comparison of volumetric cooling effect (CE _v) among all studied composites/CO ₂ and Maxsorb III/CO ₂ pairs at evaporator temperature 15°C with function of desorption temperature.....	182

List of Tables

Table 1.1	Features of widely used refrigerants according to IPCC 5 th assessment report 2014 [19].	5
Table 1.2	Direct GHG emissions rate by refrigeration and air-conditioning sector [23].	6
Table 2.1	Porous properties of ACs used for adsorption heat pump application.	20
Table 2.2	Comparison of surface area and total pore volume of the activated carbon derived from various wood based biomass [40].	22
Table 2.3	Thermal conductivity of some commonly used AC reported in literature.	27
Table 2.4	Average value of heat of adsorption (Q_{st}) of AC/ethanol and AC/CO ₂ pairs.	29
Table 2.5	Specific heat capacity of ACs [74].	30
Table 3.1	Elemental compositions of waste palm trunk (WPT) and mangrove (M).	45
Table 3.2.	Elemental compositions of carbonized WPT and mangrove at 500°C.	49
Table 3.3	Series of AC samples are prepared from WPT and M by changing carbonization and activation conditions.	51
Table 3.4	Pore structural parameters of WPT and mangrove-derived ACs that prepared at various activation conditions.	56
Table 3.5	Composition and porous properties of AC powder (Maxsorb III) [31,44,126]	63
Table 3.6	Thermo-physical properties of EC500.	63
Table 3.7	Technical specifications of graphene H-grade (H25) and C-grade (C750) [127].	64
Table 3.8	Thermo-physical properties of PVA.	65
Table 3.9	List of prepared consolidated composites.	67
Table 3.10	List of prepared consolidated composites.	68
Table 3.11	Composition and porous properties of the developed consolidated adsorbent samples.	74
Table 3.12	BET surface area and pore volume of Maxsorb III and studied composites.	80
Table 3.13	Porous properties and thermal conductivity of the studied composite.	94
Table 4.1	Thermo-physical properties of ethanol.	100

Table 4.2	Fitting parameters of the studied isotherm models for ethanol adsorption onto WPT-AC and M-AC adsorbents.	109
Table 4.3	Adsorption kinetics parameters of WPT-AC/ethanol and M-AC/ethanol pairs.	116
Table 4.4	Parameters of Arrhenius equation for studied pairs.	117
Table 4.5	Isotherm parameters of ethanol adsorption onto of the studied composites.	120
Table 4.6	Fitting parameters of the studied isotherm models for studied composites/ethanol pairs.	126
Table 5.1	Thermos-physical properties of carbon dioxide (CO ₂).	137
Table 5.2	Fitting parameters of the studied isotherm models for biomass-derived ACs/CO ₂ pairs.	146
Table 5.3	Comparison of effective uptake of the present study with numerous pairs of literature data at evaporation, adsorption, and desorption temperature are 15, 28 and 85°C, respectively.	148
Table 5.4	Fitting parameters of the isotherm models for CO ₂ adsorption onto the composite adsorbent.	154
Table 5.5	Fitting parameters of the studied isotherm models for biomass-derived ACs/CO ₂ pairs.	159
Table 6.1	Adsorption uptake and cycle performance of the studied adsorbents using ethanol and CO ₂ for cooling applications.	183

Nomenclature

b_0	equilibrium constant [kPa ⁻¹ or MPa ⁻¹]
C_p	specific heat capacity at constant pressure [J g ⁻¹ K ⁻¹]
d	small penetration depth [mm]
D_s	surface diffusion coefficient [m ² s ⁻¹]
E	adsorption characteristic energy [kJ mol ⁻¹]
F_0	geometric parameter for adsorbent particle shape [-]
h	heterogeneity constant in Tóth equation [-]
h_f	fluid enthalpy [kJ kg ⁻¹]
h_{fg}	latent heat of vaporization [kJ kg ⁻¹]
k	Freundlich constant [-]
k	fitting parameter of modified D-A equation [-]
L	sample thickness [mm]
LR	leakage rate [%]
M	molar mass [g mol ⁻¹]
n	exponent of D-A equation [-]
N	number of observation [-]
P	pressure [kPa or MPa]
P_c	pressure at critical point [kPa or MPa]
P_s	saturation pressure [kPa or MPa]
Q	heat energy [J]
Q_{st}	isosteric heat of adsorption [kJ kg ⁻¹]
q	volumetric adsorption uptake [cm ³ g ⁻¹]
q_0	maximum volumetric adsorption capacity [cm ³ g ⁻¹]
R	gas constant [J mol ⁻¹ K ⁻¹]
RC	refrigerant charge [kg kW ⁻¹]

R_p	radius of the adsorbent particle [m]
t	time [ms or s or min]
T	temperature [°C or K]
T_C	temperature at critical point [°C or K]
V_m	molar volume [cm ³ g ⁻¹]
v_m	pore volume of the adsorbent [cm ³ g ⁻¹]
V_t	specific volume of liquid carbon dioxide [cm ³ g ⁻¹]
W	equilibrium uptake [g g ⁻¹ or kg kg ⁻¹]
W_0	maximum equilibrium uptake [g g ⁻¹ or kg kg ⁻¹]

Greek Symbols

α	thermal diffusivity [m ² s ⁻¹]
α^*	thermal expansion of the adsorbed gas [K ⁻¹]
ρ	density [kg m ⁻³]
τ	time constant [ms or s or min]
ΔW	effective uptake [-]

Subscripts

ad	adsorbent
ads	adsorption
atm	atmospheric
CC	Clausius-Clapeyron
c	condenser
$cond$	condenser
des	desorption
e	evaporation
$evap$	evaporator
e,a	ending, adsorption
e,d	ending, desorption
max	maximum

<i>min</i>	minimum
<i>ref</i>	refrigerant
<i>s</i>	saturation
<i>sat</i>	saturation
<i>sens</i>	sensible
<i>s, a</i>	start, adsorption
<i>s, d</i>	start, desorption

Abbreviations

AC	activated carbon
ACs	activated carbons
COP	coefficient of performance
GWP	global warming potential
PIL	polymerized ionic liquid
SCE	specific cooling effect

Chapter 1

Introduction

Conventional heat pump systems are often considered as one of the major contributors to environmental problems due to the usage of chlorofluoro, hydrochlorofluoro, and hydrofluoro carbon-based refrigerants. Furthermore, it also consumes a considerable amount of electricity. Earlier versions of refrigerants used to have high ODP as well as GWP. However, next generation refrigerants that are environmentally benign with excellent thermos-physical properties are still under development stage. This chapter includes the review of the historical development of refrigerants, their environmental impacts and observes the viewpoint for present options in terms of Montreal Protocol, Kyoto Protocol, and EU F-gas regulation. The direct CO₂ emission per year from air-conditioning and refrigeration sectors due to the system leakage is assessed. It also examines the significant contributors of CO₂ emission in every year among the various sectors for providing per kilowatt cooling effect. Finally, this chapter explains the motivation of this thesis to adsorption heat pumps systems. The objectives and outline of this thesis are presented in the later part of the chapter.

1.1 Background

Climate change as a consequence of global warming and ozone layer depletion is one of the most serious threats the world is facing today [1]. The greenhouse gas concentration in the troposphere is increasing especially due to the manmade activities, like transportation, industrialization and power generation etc. This gas absorbs the infrared radiation which results in increased atmospheric temperature known as climate change. The radiation energy is measured by global warming potential (GWP) which is defined as the infrared radiation amount that the gas can absorb, relative to carbon dioxide (GWP = 1), integrated over a time interval of 20, 100 and 500 years [2]. Refrigerant used in the conventional heat pump systems is responsible for the global warming and ozone layer depletion. Total equivalent warming impact (TEWI) is a tool for appropriate quantify of a refrigerant impact to global warming. Hwang et al. [3] defined two types of global warming effects. Firstly, the direct global-warming potential which is owing to the leakage

of refrigerants and other pollutants from the systems. Secondly, the indirect global-warming potential which is related to the carbon dioxide emission during combustion of fossil fuels (oil, natural gas, and coal) to generate electricity. The combined effect of direct refrigerant emission and energy consumption of a heat pump system are acknowledged as TEWI [2].

About 11 km above the earth surface ozone layer exist in the atmosphere and acts as a safeguard for earth for thousands of years [2]. Ozone layer consists of ozone (O_3) molecules with a high concentration. All the harmful ultraviolet rays of the sun are efficiently absorbed by this layer. Any kind of demolition of this layer can cause significant destruction to the environment and the life on earth [2].

Heat pump technologies play a significant role in our everyday life. It offers not only comfortable and healthy living and working atmospheres but also considered as certainties for preserving food and medicine at extreme weather [2]. With the change of lifestyle and economic solvency, the demand and supply of such systems have gradually increased. However, conventional air-conditioning (A/C) and refrigeration systems consume huge electricity and use refrigerants like chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), which possesses high global warming potential (GWP) as well as ozone layer depletion potential (ODP) [4]. Currently, Hydrofluorocarbons (HFCs) are considered as an alternative to the CFCs and HCFCs in A/C systems. This refrigerant has no ODP, but it has high GWP. Many studies [5–8] have been focused on hydrofluoro-olefins (HFOs) as it has very low GWP. Fig. 1.1 shows the schematic diagram of a typical vapor compression cycle comprises the following four essential elements: an evaporator, where the refrigerant evaporates by taking heat from the external environment. A mechanical compressor, which sucks the evaporated vapors to compress and expel it at a higher pressure and temperature. The compressor consumes a considerable amount of electrical energy. A condenser, in which the vapor refrigerant condenses by transferring a certain amount of heat to the outdoor environment. An expansion valve, through which the liquid refrigerant returns back to the evaporator, with a lower pressure to repeat the cycle.

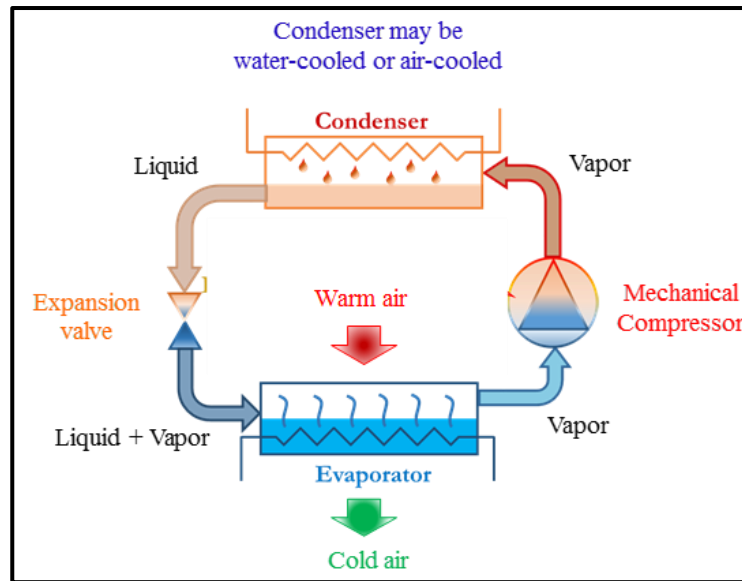


Fig. 1.1 Schematic diagram of a conventional heat pump system.

Notable researchers are also focusing natural refrigerants such as water, ethanol, and CO₂ for thermally driven adsorption A/C and refrigeration systems [9–18]. This technology with natural refrigerants is considered as an alternative for the conventional systems in the near future.

1.2 Historical development of refrigerants

The refrigerant is the heat transfer fluid in refrigeration and air-conditioning systems. It absorbs heat from one area, such as space, which needs to be cooled, and reject heat into outdoors, usually by evaporation and condensation, respectively. According to the information available in open literature, Oliver Evans in 1805 suggested using evaporative two-phase fluid in a closed cycle to freeze water into ice. He proposed a system that can produce a cooling effect by evaporating ether. Jacob Perkins and Richard Trevithick are influenced by that idea and proposed an air-cycle system for refrigeration in 1828. Perkins in 1830 invented a vapor the compression machine by using sulfuric (ethyl) ether as a refrigerant. The common refrigerants for the first generation (1830-1930s) were familiar solvents and other volatile fluids whatever worked as a refrigerant at that time. Almost none of those refrigerants were environment-friendly because of flammability, toxicity, or both and some were highly reactive to the heat exchanger material. Some common early refrigerants were ethers, CO₂, NH₃, SO₂, HCs, H₂O, CCl₄ [19]. The second-generation (1931-1990s) refrigerants were famed by a shift to fluoro-chemicals for safety and

durability. Midgley and Henne invented Freon in 1928 as a refrigerant. Well-known refrigerants in the second generation were CFCs and HCFCs (R11, R12, R22, R502) and NH_3 . Commercial production of R12 started in 1931 followed by R11 in 1932. Ammonia (NH_3) is one of the older types of refrigerant and remains until now, the most prevalent refrigerant in large, industrial systems particularly for beverage, storage, and food. CFCs are responsible to create the hole in the ozone layer. The Vienna Convention and resulting Montreal Protocol designed to phase out the production of ozone-depleting substances (ODSs). Therefore, the primary focused of the third generation refrigerant (1990-2010s) was HCFCs and HFCs for the longer term, such as R123, R134a, R410A, R404A, many blends and also NH_3 [19]. Actually, most of the third generation refrigerants had ODP and high GWP. Therefore, fourth generation (from 2010 to now) is mainly focused on zero ODP and low GWP refrigerants. Fig. 1.2 represents the schematic drawing of refrigerant progression.

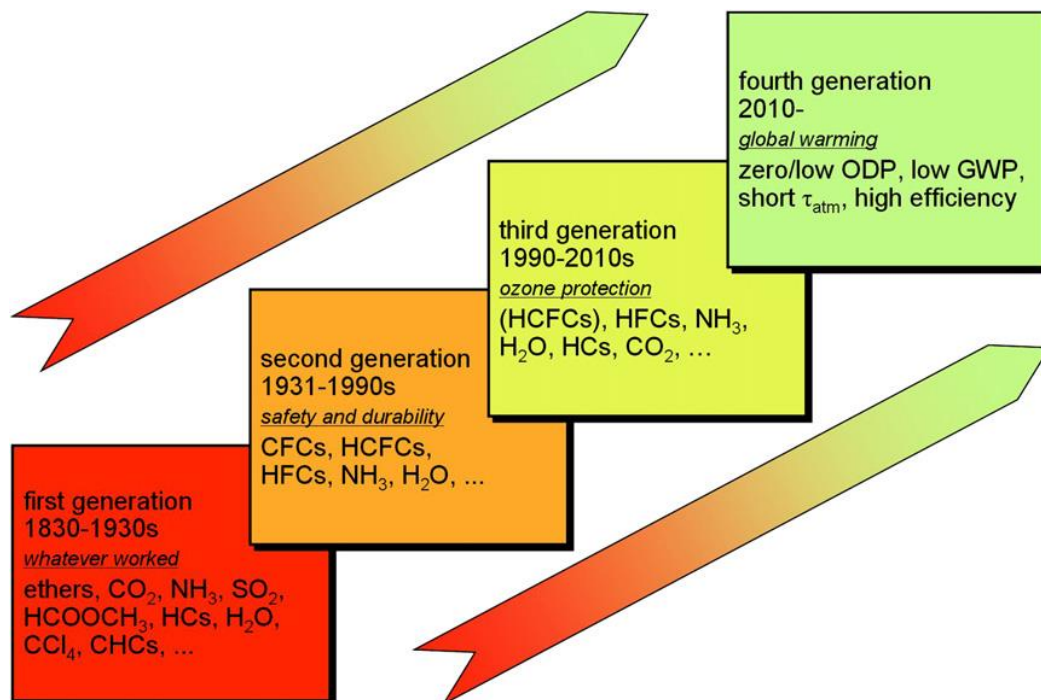


Fig. 1.2 Refrigerant progression [19].

1.3 GWP and ODP of commonly used refrigerants

The environmental effects and safety classification of widely used refrigerants are shown in Table 1.1. Both CFCs and HCFCs have ODP and GWP. However, HFCs have only GWP. After the Montreal Protocol signed in 1987, the CFCs and HCFCs are gradually banned due to their harmful effect on the ozone layer. Most of the existing refrigerants in

commercialized A/C systems are HFCs. Although HFCs does not have an impact on the ozone layer, they have GWP. Research has been intensified to find alternative refrigerants to conventional HFCs after adopting the above-mentioned international protocols.

Table 1.1 Features of widely used refrigerants according to IPCC 5th assessment report 2014 [19].

Compositional group	Refrigerant number	Chemical formula	Ozone depletion potential (ODP)	Global warming potential (GWP)	Safety group
CFCs	R11	CCl_3F	1	4660	A1
	R12	CCl_2F_2	1	10200	A1
	R113	$\text{CCl}_2\text{FCClF}_2$	0.8	5820	A1
	R114	$\text{CClF}_2\text{CClF}_2$	1	8590	A1
	R115	CClF_2CF_3	0.6	7670	A1
HCFCs	R22	CHClF_2	0.055	1760	A1
	R123	CHCl_2CF_3	0.02	79	B1
	R124	CHClFCF_3	0.022	527	A1
	R142b	CH_3CClF_2	0.065	1980	A2
HFCs	R23	CHF_3	0	12400	A1
	R32	CH_2F_2	0	677	A2L
	R125	CHF_2CF_3	0	3170	A1
	R134a	$\text{CF}_3\text{CH}_2\text{F}$	0	1300	A1
	R143a	CH_3CF_3	0	4800	A2
	R152a	CH_3CHF_2	0	138	A2
	R410A	R32 (50%) R125 (50%)	0	1900	A1

1.4 Assessment of global warming potential

Gschrey et al. [20] mentioned that the impact of fluorinated gases (F-gases) to global warming would rise from roughly 1.3% (2004) to 7.9% (2050) of expected total CO₂ emissions [21,22]. Still, most of the refrigerants used in refrigeration and A/C systems are F-gases. Leakage of refrigerant gases from these systems influences the environment in two ways (Koronaki et al. [23]). Firstly, there is a direct effect due to the GWP of the leaked gas, and secondly, there is an indirect effect owing to the energy consumption by the system (Grace et al. [20]). In this study, the direct effect due to high GWP of refrigerants has been considered. The leakage rate of refrigerant is different for different systems. According, UK Greenhouse Gas (GHG) inventory for 2007, Table 1.2 represents the leakage rates for the different types of refrigeration and A/C system [23].

For investigating, the direct GHG emission four cases such as room A/C, domestic refrigeration, commercial refrigeration, and industrial refrigeration are considered. Furthermore, HCFC (R22), HFCs (R410A, R134a, and R32), HFO (R1234yf, R1234ze) and natural (R600a) refrigerants have been used for the assessment of direct global warming impact. Refrigerant charge into system depends on system type and capacity. Poggi et al. [24] mentioned the specific charge amount per kW capacity based on the size of the heat pump systems. Fig. 1.3 shows the specific charge (kilogram per kilowatt) amount in complete systems for different applications using different refrigerants [25]. It can be observed that initial charging amount of refrigerant in different kinds and sizes are different.

Table 1.2 Direct GHG emissions rate by refrigeration and air-conditioning sector [23].

Type of equipment	Annual leak rate
Domestic refrigeration	0.30%
Stand-alone commercial applications	2.00%
Medium & large commercial applications	11.00%
Industrial refrigeration	8.00%
Residential/commercial air-conditioner	8.5%

The direct global warming impact per kW capacity has been calculated using equation (1.1) [25]. Leakage occurs mostly near the compressor side. It is happening when

the pressure of gas increased; it is much higher than atmospheric pressure compressed by the compressor. In this study, condenser temperature has been considered 40°C to calculate the pressure of leakage gas, as it is an isobaric process. Therefore, leakage rate differs from one refrigerant to another, as their operating pressure is different.

$$GWP_{direct} = RC \times LR \times GWP_{ref} \quad (1.1)$$

where GWP_{direct} denotes the direct global warming impact, RC is the refrigerant charge (kg kW⁻¹), LR is the leakage rate of initial charge (per year), and GWP_{ref} represents the GWP of refrigerant.

Fig. 1.4 represents direct emission amount of CO₂ per kW/year for the residential A/C system. It can be seen that R22 shows high emission rate with contains ODP value. HFC group (R410A, R134a, and R32) does not contain any ODP, however high GWP emission rate has been observed. It is highlighted that R32 shows quite low CO₂ emission compared to other HFCs, which is recently promising worldwide. HFOs and natural refrigerant emit almost zero emission. Therefore, HFOs and natural refrigerants are potential for next generation heat pump technology. However, due to low system performance and flammability, these refrigerants need further study to use in every sector. A similar trend has been observed for domestic, commercial and industrial refrigeration systems. Fig. 1.5 shows the comparison of direct emission amount of CO₂ per kW/year for the various system. It is observed that industrial and commercial refrigeration systems are a significant contributor to direct emission of GHG because of the high leakage rate and high amount of initial charging of refrigerant. It can be concluded here that conventional heat pump technology still emits high rate of CO₂ to the environment although current refrigerants possess low GWP. International protocols such as Kyoto protocol are continuously forcing the heat pump industries for using low GWP refrigerants and shift to natural refrigerants.

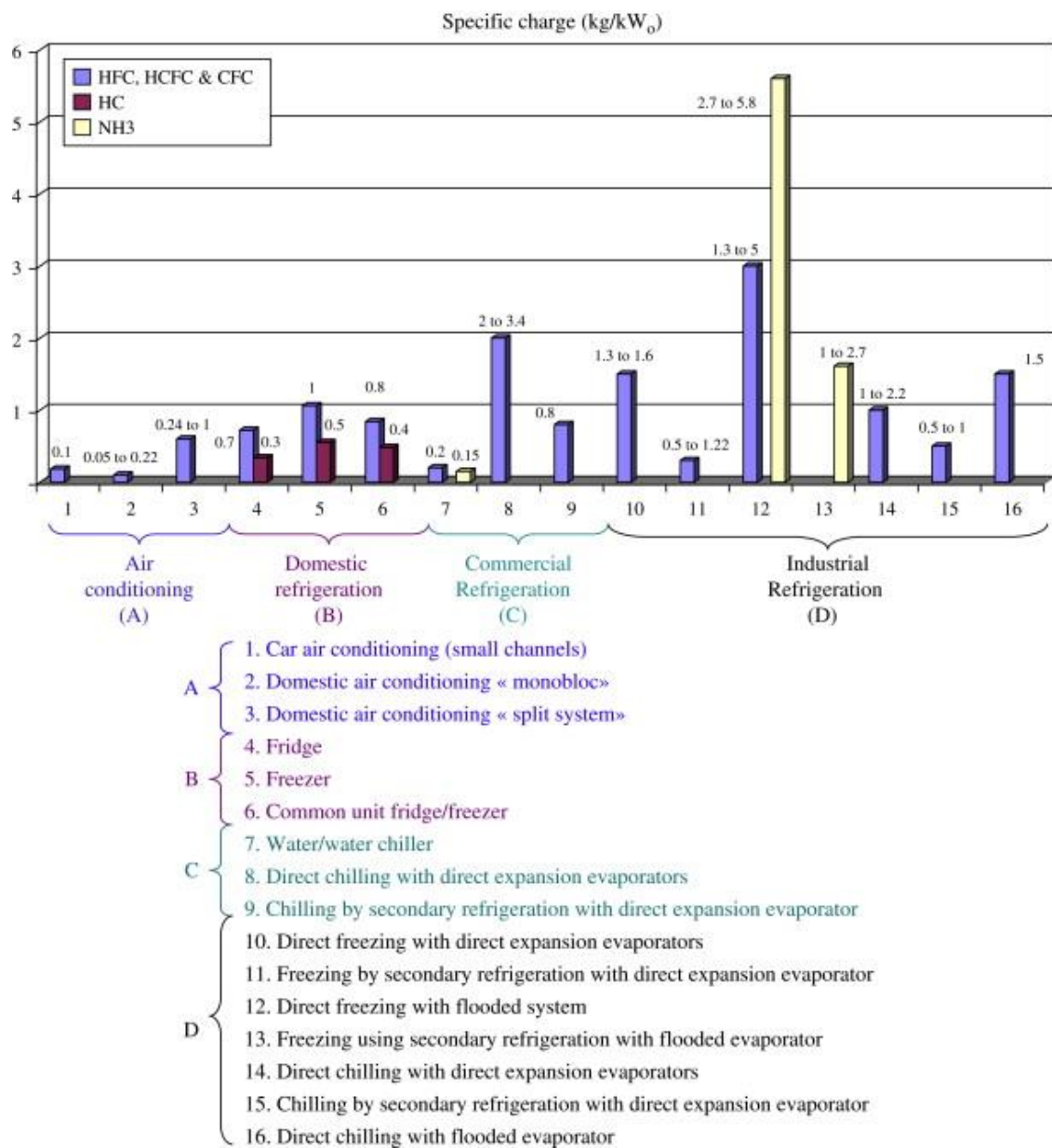


Fig. 1.3 Specific charge amount in complete systems for different applications using different refrigerants [24].

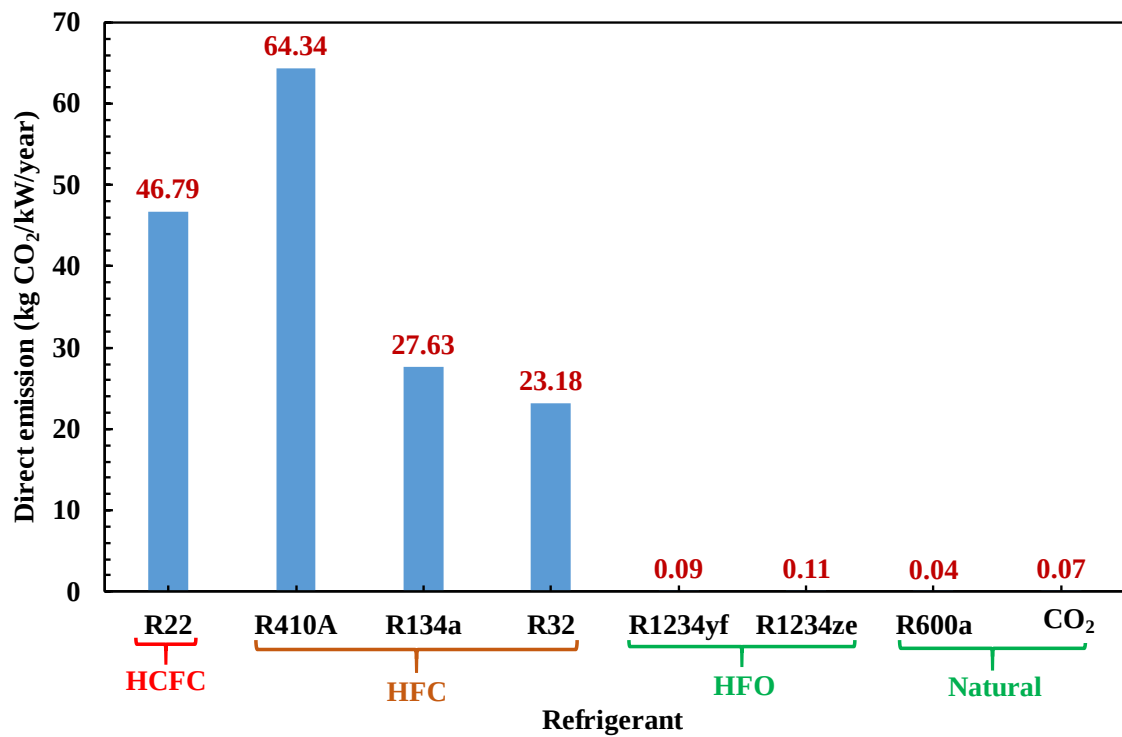


Fig. 1.4 Direct emission amount of CO₂ per kW/year from the residential air-conditioner.

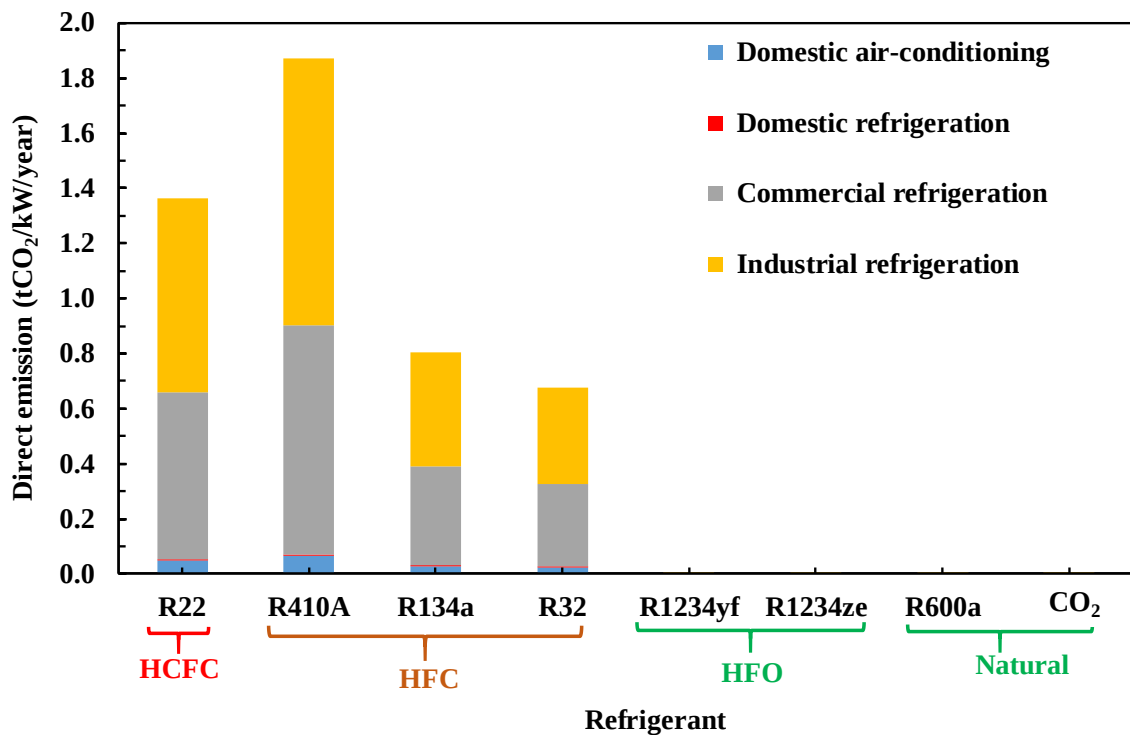


Fig. 1.5 Comparison of direct emission amount of CO₂ per kW/year from the various system.

1.5 Motivation

Above studies indicated that conventional heat pump technologies using HCFC and HFC based refrigerants emit an enormous amount of CO₂ in every year. Based on the international regulations of the environment (Kyoto protocol, Vienna Convention, and Montreal Protocol) CFCs and HCFCs phase-out have been agreed and make timeframe for entirely ban HCFC from developed and developing by 2020 and 2030, respectively. Furthermore, countries are seeking to limit HFCs use to meet its legally binding greenhouse gas emissions targets by the Kyoto protocol. At the same time, this system consumes a considerable amount of electricity, which is also one of the significant issues currently all over the world. Refrigeration and air-conditioning systems are responsible for roughly 30% of total worldwide energy consumption [26,27]. For a residential building, almost half of the primary energy is consumed by the cooling/heating technology [28]. Due to the energy consumption and uses of environmentally harmful refrigerants in conventional heat pump system, research on the alternative heat pump system has been getting momentum. Consequently, adsorption heat system (AHP) has been considered as a potential, next generation, and alternative to conventional system as it can directly utilize the low temperature waste heat and natural refrigerant. The important advantages of the adsorption heat pumps can be described as follows:

- can be driven by thermal energy
- can operate by low temperature (less than 100°C) thermal energy sources such as industrial waste heat, solar thermal heat, and car exhaust heat.
- natural refrigerant or low GWP refrigerant can be used as a working fluid
- no need electricity
- systems are environmentally friendly
- operate without noise and vibration having a simple working principle
- do not require frequent maintenance and long life time

Therefore, above-mentioned advantages of AHP (non-conventional) systems over conventional system make me fascinating to do research on further performance improvement from its current position for accelerating the widespread use of this technology.

1.6 Aims and objectives of the thesis

The aims of this research are directed towards the development of high performance parent (activated carbon) and composite adsorbents for application to waste heat driven adsorption heat pump systems. The research mainly stresses on the synthesis and characterization of the high surface area and pore volume contained ACs from the two precursor biomass materials. Secondly, it includes synthesis and characterization of composite adsorbents for the improvement of thermal conductivity of AC. Finally, thesis presents the feasibility study of developed ACs and composites for application to ethanol and CO₂ based non-conventional heat pump (AHP) system. The biomass-derived ACs with high pore volume contributes to make higher effective or net uptake. In addition, composites using the additives could enhance thermal conductivity and volumetric adsorption uptake. As a result, developed adsorbent/refrigerant pairs will assist to make a compact with high performance AHP systems. To achieve the above mentioned research aim, the objectives of the present thesis are as follows:

1. Review of fundamental characterization of adsorbents, theoretical and experimental research work on activated carbon based adsorption heat pump systems.
2. To synthesis of a series of highly porous ACs from the two kinds of biomasses through carbonization followed by KOH activation. Waste palm trunk (WPT) and mangrove (M) are employed as a renewable and cheap source of precursor material for synthesis of ACs
3. To do series of experiments that enable selecting the optimum activation conditions corresponding to high BET surface area and pore volume contained ACs.
4. To investigate the N₂ adsorption/desorption isotherm, porous properties and thermal conductivity of biomass-derived ACs.
5. To synthesis the activated carbon based composite adsorbents using expanded graphite (EG) and graphene nanoplatelets (GNPs) for improvement of thermal conductivity of AC.
6. To synthesis AC composites using polymerized ionic liquid as a binder instead of conventional binders.
7. To investigate the N₂ adsorption isotherm, porous properties and thermal conductivity of composite adsorbents.

8. To measure the adsorption isotherm and kinetics of environment friendly refrigerant ethanol and CO₂ onto selected biomass-derived ACs and composite adsorbents using a gravimetric method based adsorption measurement unit for AHP applications.
9. To analyse the adsorption equilibrium data with various adsorption isotherms and kinetics models for each pair.
10. To investigate the performance of an equilibrium adsorption cooling cycle using biomass-derived ACs and composites/ethanol and CO₂ pairs along with Maxsorb III/ethanol and CO₂ pairs for comparison by considering a time-independent thermodynamic model.

1.7 Organization of the thesis

The thesis comprises seven chapters describing the various experiments on synthesis and characterization of developed ACs and composite adsorbents, data analysis using theoretical models, and the analysis of equilibrium adsorption cycle in order to achieve the research objectives. The arrangement of the thesis is as follows:

Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Development of adsorbent material

Chapter 4: Application to low pressure adsorption system

Chapter 5: Application to low pressure adsorption system

Chapter 6: Thermodynamic analysis of an adsorption cooling cycle

Chapter 7: Overall conclusions and recommendations

The key points of each chapter are given as follows:

Chapter 1 provides a general introduction of conventional heat pump systems, review of the historical development of refrigerants and their environmental impacts. It is also mentioned the assessment of direct CO₂ emission per year from various conventional air-conditioning and refrigeration sectors due to the system leakage. Finally, this chapter presents the motivation and objectives of the thesis

Chapter 2 gives an overview of the literature pertinent to the present research, which has three main parts. The first part provides a brief description of the adsorption

fundamentals. In the second part, fundamental characterization of adsorbent materials has been discussed following a thorough review of different techniques. Finally, a comprehensive literature reviewed on the recent status of activated carbon based adsorbents/refrigerants pairs is provided. At the end, this chapter mentions the scopes of this thesis and the approaches to reach that scopes.

Chapter 3 describes the adsorbent materials development and fundamental characterization of the adsorbents to the design the compact AHP systems. This chapter presents the synthesis of: i) waste biomass-derived highly porous ACs; ii) composite adsorbents using expanded graphite (EG) and graphene nanoplatelets (GNPs); iii) synthesis of polymerized ionic liquid (PIL) and composite using PIL as a binder. It also provides the experimental investigation of the surface characteristics including surface area, pore volume, and pore size distribution of all synthesized adsorbents. The thermal diffusivity and conductivity of all studied adsorbents are measured. The porous properties and thermal conductivity are used in identifying a suitable adsorbent for ethanol and CO₂ adsorption. Surface morphology of all synthesized biomass-derived ACs is also presented. Finally, the porous properties and thermal conductivity data are compared with the hitherto commercial AC, namely Maxsorb III.

Chapter 4 presents the experimental and theoretical studies of the applicability of selected biomass-derived ACs and composite adsorbents to the low pressure refrigerant (ethanol) based AHP systems. At the beginning of this chapter describes the experimental methods, apparatus, and procedures in determining the adsorption isotherm and kinetics of the selected parent and composite adsorbents/ethanol pair. Experiments have been carried out using a gravimetric method at adsorption temperatures ranging from 30 to 70°C and pressures ranges corresponding to the working conditions of adsorption cooling cycle for the suitable design of adsorption system. The theory of adsorption isotherm and kinetics models are then discussed. Five isotherm and two kinetics models are fitted with the experimental data of each pair to understand the adsorption characteristics of CO₂. Finally, estimated isotherm and kinetics parameters of each pair are compared to the Maxsorb III/ethanol pair.

In chapter 5, the applicability of selected biomass-derived ACs and composite adsorbents to the high pressure refrigerant (CO₂) based adsorption system have been conducted. In the beginning of this chapter describes the experimental methods, apparatus, and procedures in determining the adsorption uptake and kinetics of the ACs and

composite adsorbents/ethanol pair. Experiments have been carried out using a gravimetric method at various adsorption temperatures and pressures. The theory of adsorption isotherm models is then discussed. Three isotherm models are fitted with the experimental data of each pair to understand the CO₂ adsorption characteristics. Finally, estimated isotherm and kinetics parameters of each pair are compared to the Maxsorb III and other ACs.

Chapter 6 presents the thermodynamic analysis of an equilibrium adsorption cooling cycle using biomass-derived ACs and composites/ethanol and CO₂ pairs along with Maxsorb III/ethanol and CO₂ pairs for comparison. The performance of ideal adsorption cooling cycle has been discussed at three different evaporator temperatures, namely 5, 10 and 15°C along with a coolant temperature of 30°C and heat source temperatures ranging from 45 to 90°C by considering a time-independent thermodynamic model.

In Chapter 7, the thesis ends with the significant findings where the originality and contribution of the author and recommendations for future improvement have been made. It is concluded that the biomass-derived ACs are promising parent adsorbent for heat pump application compared to any other ACs that are currently available from the viewpoints of porous properties, uptake (ethanol and CO₂), and renewability and cheap source of precursor material. In addition, composite adsorbents also show potential because of its high thermal conductivity and volumetric uptake. It is also observed graphene nanoplatelets (GNPs) contained composites are superior to expanded graphite (EG) contained composites in terms of thermal conductivity enhancement. Therefore, the utilization of biomass-derived ACs and composites as adsorbents could lead to the compact design of adsorbent heat exchanger and hence reduces the size of adsorption heat pump systems.

Chapter 2

Literature review

Adsorption heat pump (AHP) systems are an environmentally benign alternative for the conventional vapor compression system. However, for widespread disseminating of AHP technology, the performance of the system has to be improved. Adsorbent plays one of the key roles for the improvement of efficiency. So, high performance adsorbent with details characterization is needed for developing AHP system. Consequently, this whole thesis has been focused on the development of adsorbent materials with enhanced adsorption uptake and thermal conductivity. For this purpose, author studies the adsorption cooling system and adsorbent materials with its characterization. Finally, the author finds the limitations and tries to improve the characteristics of the adsorbent materials in the subsequent chapter. Therefore, this chapter presents the review of adsorption cooling systems with a focus on activated carbon based adsorbent/refrigerant pairs. The literature review has been broadly classified into the following categories:

- i) Adsorption cooling system: this includes working principle, phenomena of the adsorption process, adsorbent and adsorbate characteristics.
- ii) Fundamental characterization: this includes the equilibrium uptake measurement, measurement of instantaneous uptake or adsorption kinetics and thermo-physical characteristics determination.
- iii) Adsorbent/refrigerant pairs: investigation of adsorption uptake, kinetics, and performance of parent activated carbon and composite/refrigerant pairs.

In the following sections, each of the above mentioned points are extensively reviewed to conclude the optimum enhancement techniques for the adsorption cooling systems.

2.1 Adsorption cooling system

2.1.1 Adsorption process

Adsorption phenomenon has been known for a long time. It can be physi-sorption or chemi-sorption. Physical adsorption is the adherence of molecules/atoms of gas on the

solid surface held due to van der Waal's forces. The key element in adsorption process is porous solid medium with a huge surface area and large pore volume and hence high adsorption uptake [29].

Adsorption of ethanol vapour onto activated carbon (AC) is an instance of a physisorption process. In this process, the ethanol vapour (adsorbate) molecules diffuse through the micropores (pore diameter < 2 nm) of AC (adsorbent) and attach to its surface [30] (see Fig. 2.1 a)).

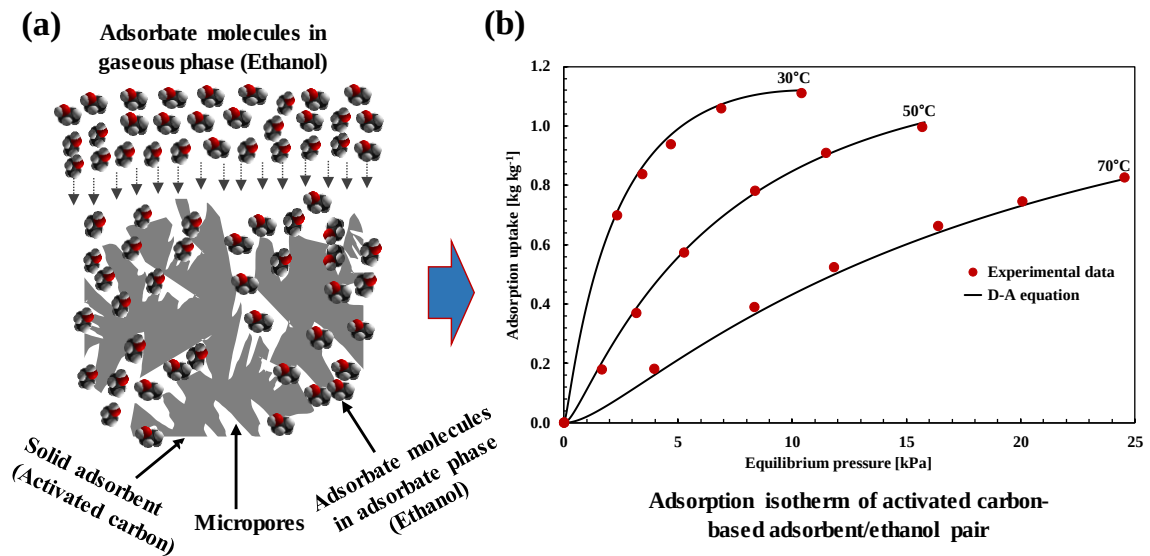


Fig. 2.1 a) Schematic of adsorption process b) Adsorption isotherms.

The amount of ethanol uptake is governed by the vapor pressure of ethanol (adsorbate) and temperature of AC (adsorbent). The uptake of any adsorbent/adsorbate pair at particular adsorbent temperature is known as isotherm and can be represented on a pressure-uptake plane plot. Fig. 2.1 (b) describes the adsorption isotherm plot for AC based adsorbent/ethanol pair. It is observed that at low temperature and high pressure lead to high uptake whereas at low pressure and high temperature leads to poor uptakes. This adsorption uptake variation as a function of pressure and temperature is the origin of the thermal compression process. The following section explains the working principle of an adsorption cooling cycle.

2.1.2 Working principle of adsorption cooling systems

The working principle of adsorption cooling system is similar to conventional vapor compressor system. The fundamental difference is that mechanical compressor in the conventional system is replaced by two bed heat exchangers which is called thermal compressor since it can be driven by thermal energy. Various kinds of adsorbents such as silica gel, zeolite, activated carbon, metal-organic-framework are used in bed for adsorbed refrigerants gas molecules. Natural working fluids such as water, ethanol, methanol, CO₂ are used as a refrigerant instead of using environmentally harmful refrigerant (HCFCs, HFCs). Fig. 2.2 shows the schematic diagram of adsorption cooling system, which composes an evaporator, two adsorber/desorber heat exchangers that are act as a thermal compressor and a condenser. The adsorber and evaporator are connecting through a throttling valve to keep the pressure difference.

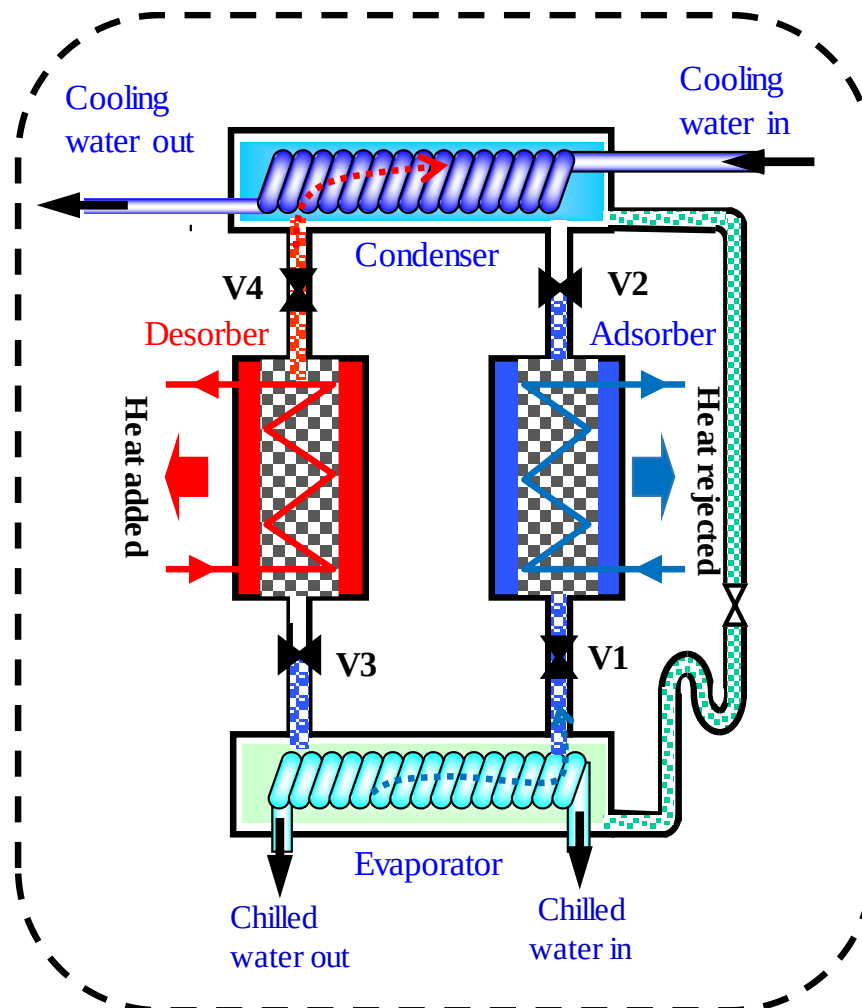


Fig. 2.2 Schematic diagram of basic adsorption cooling system.

The thermodynamic relation among pressure, adsorption temperature, and amount of refrigerant adsorbed per unit mass of adsorbent at equilibrium state can be expressed using P-T-W (pressure-temperature-concentration) diagram. Fig. 2.3 illustrates the thermodynamic cycle of the basic adsorption cooling system. It consists of four steps which are isosteric heating (preheating), isobaric desorption (desorption), isosteric cooling (pre-cooling), and isobaric adsorption (adsorption) as shown in Fig. 2.3.

In adsorption process ($1 \rightarrow 2$), the pressure is kept constant at P_{evap} and adsorber bed is connected to the evaporator. The refrigerant vapor evaporates in the evaporator and adsorbs by the adsorbent in the adsorber. The refrigerant concentration in the adsorber increases from W_{min} to W_{max} . During the adsorption process, the heat of adsorption is released which is removed from the adsorber by applying cooling water.

In pre-heating ($2 \rightarrow 3$) process, the adsorbent is isolated from the condenser and evaporator. The adsorber temperature increases by continuously heating with the high temperature external heat source. In this step desorption of refrigerant vapor does not occur and hence the pressure increases from P_{evap} to P_{cond} .

In desorption process ($3 \rightarrow 4$), the heating process is continued, and the valve between the adsorber and condenser is opened. Desorption process is started, and the refrigerant vapor is liquefied inside condenser. It is then returned to the evaporator through the expansion valve. In this time, refrigerant concentration into adsorbent decreases from W_{max} to W_{min} , and the pressure remains constant.

During the pre-cooling process ($4 \rightarrow 1$), the valve between the condenser and adsorber is closed, and the adsorber is cooled by cooling load. In this step temperature of the adsorber decreases to the adsorption temperature and the pressure decreases from P_{cond} to P_{evap} .

Therefore, during the adsorption process, the refrigerant is evaporated by gaining heat from the environment and hence the cooling effect of this cycle occurs. Conversely, the heating effect occurs when the refrigerant is condensed by releasing heat to the environment.

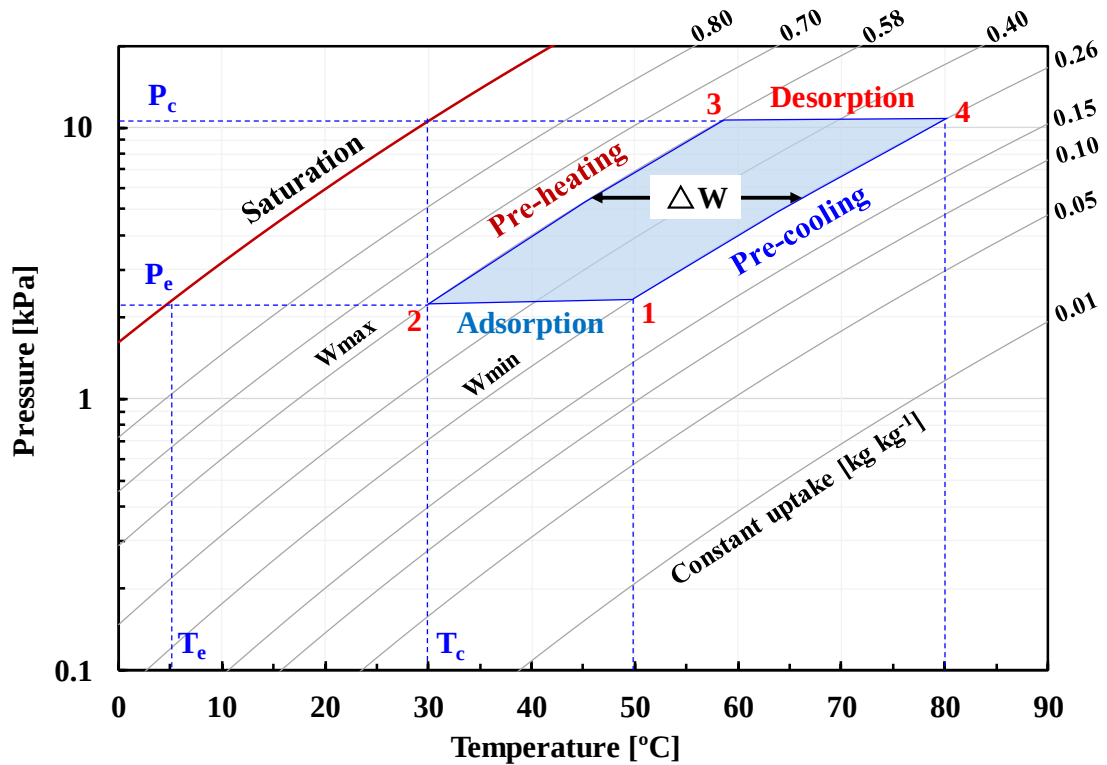


Fig. 2.3 Thermodynamic cycle (P-T-W diagram) of a basic adsorption cooling system.

2.1.3 Adsorbent

The adsorption working pair is the vital part of the adsorption cooling cycle. The choice of any pair of adsorbent/adsorbate for cooling applications depends on certain required features of their constituents. Followings are the key considerations influencing the choice of a suitable adsorbent.

- i. Adsorption of significant amount of the adsorbate under low temperature conditions.
- ii. Desorption of most of the adsorbate when exposed to thermal energy.
- iii. Possession of high latent heat of adsorption compared to sensible heat.
- iv. No deterioration with age or use.
- v. Non-toxic and non-corrosive.
- vi. Low cost and widely available.

Activated carbon (AC) is a promising adsorbent for adsorption of ethanol and CO₂ among the various adsorbents such as silica gel, and zeolites. Because AC possesses very

high surface area and pore volume which implies mean higher affinity to the adsorbed gas molecules. Table 2.1 shows the porous properties and precursor material of ACs that were already developed by numerous researchers or companies and used for adsorption cooling application.

Table 2.1 Porous properties of ACs used for adsorption heat pump applications.

Adsorbent	Surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore size [nm]	Precursor material	Reference
Maxsorb III	3045	1.7	1.12	petroleum coke	[31]
H ₂ -Maxsorb III	3029	1.73	1.15	petroleum coke	[32]
KOH-H ₂ - Maxsorb III	2992	1.65	1.11	petroleum coke	[32]
KOH4-PR	3060	1.9	1.25	phenol resin	[14]
KOH6-PR	2910	2.53	1.78	phenol resin	[14]
AC-35.4	1200	0.69	2.3	-	[33]
ACF	2200	1.0	2	-	[34]
AX21	3106	1.29	-	petroleum pitch	[35]
BPL	1150	0.43	-	coal	[36]
Norit R1 Extra	1450	0.47	-	peat	[36]
Activated carbon A	1207	0.54	-	coconut shell	[36]
A10 fiber	1200	0.53	-	petroleum pitch	[36]
ACF (A-20)	1900	1.028	2.16	-	[37]
ACF (A-15)	1400	0.765	2.175	-	[37]
AC-CSAC	804.02	0.43	1.76	coconut shell	[38]
Norit RB3	978.04	0.51	2.10	charcoal	[39]
Norit Darco (100 mesh size)	876.45	0.73	3.33	charcoal	[39]
Norit Darco (12 × 20 US mesh size)	462.67	0.50	4.28	charcoal	[39]

Above literature, review indicated that until now most ACs used for AHP applications are derived from non-renewable sources such as peat, petroleum coal, coke, and pitch. There are very few ACs derived from biomass or waste biomass for AHP applications. At the beginning of the development of ACs, coal was considered an affluent source of carbon and as the best precursor material for the production of AC with the large surface area. However, coal mines are limited and non-renewable. Consequently, this approach shifted towards renewable resources, such as biomass or any carbon-rich waste for AC production. All natural resources that can be grown through the agricultural activities in short rotation of cultivation period considered as the renewable resources and most of the waste biomasses contain a high carbon content, which make them potential precursor for AC production [40].

Many researchers synthesized ACs from biomasses for various other applications, and no one significantly focused on AHP application. Although biomass-derived ACs contains quite a high amount of ash compared to commercially coke derived ACs, it is considered not to be a severe problem, unlike the electrochemical applications. Table 2.2 shows the surface area and pore volume of ACs dreived from varoius wood biomasses for various applications.

Table 2.2 Comparison of surface area and total pore volume of the activated carbon derived from various wood based biomass [40].

Raw material	BET surface area [$\text{m}^2 \text{g}^{-1}$]	Total pore volume [$\text{cm}^3 \text{g}^{-1}$]
Pine sawdust	352	0.194
Coniferous wood (S4A6)	387	0.24
Eucalyptus wood (CS_2)	582	0.42
Olive-tree wood	904	1.198
Eucalyptus wood (H_2SO_4)	979	0.72
Uruguayan Eucalyptus wood	990	0.4
Indian Shrub wood	1024	0.572
Walnut wood	1033	0.686
Almond tree pruning	1080	0.95
Fir wood	1131	0.87
Pine sawdust	1390	0.77
Eucalyptus wood	1491	0.8
Poplar wood (Na_2CO_3)	1579	0.856
Acacia mangium wood	1767	1.59
Birch wood	1826	1.461
Oak wood	2553	1.611
Paulownia wood	2736	1.387
Fir wood	2821	1.73

2.1.4 Adsorbate

The adsorbate as known as refrigerant is the heat transfer fluid in AHP systems. It absorbs heat from the room space that needs to be cooled, and reject heat into outdoors, usually by evaporation and condensation, respectively. The adsorbate or refrigerant should have the following properties [41,42].

- i. high latent heat of vaporization and low specific volume.
- ii. small molecular size to enable it to be adsorbed into the adsorbent.
- iii. thermally stable with the adsorbent at the cycle operating temperature ranges.
- iv. non-toxic, non-corrosive and non-flammable.

Fluorocarbon refrigerants used in conventional heat pump systems contribute up to 50% of the chlorofluorocarbon emission in the atmosphere and thus accounts for about 33.3% of the greenhouse effect as reported by Edmunds et al. 1987. Because of the Montreal Protocol on substances that lessen the ozone layer, entirely halogenated fluorocarbon refrigerants recently used on a large scale in air-conditioning/refrigeration industries are to be phased out. To preserve the environment, environmentally refrigerants such as ethanol and CO₂ have been used widely for adsorption cooling system.

2.2 Fundamental characterization

For any adsorbent/adsorbate pair, the equilibrium adsorption uptake and the instantaneous uptake are the two utmost fundamental characteristics, which help to determine the promising adsorption pair for particular application. The equilibrium uptake or capacity of any pair is usually characterized as an isotherm on a pressure versus uptake plane plot. Conversely, the instantaneous uptake (adsorption kinetics) signifies the time requisite to achieve a given uptake. Along with these parameters, the thermo-physical properties like porous properties of adsorbent, the heat of adsorption of particular pair, specific heat capacity of adsorbent and thermal conductivity of adsorbent are needed to know in order to develop an adsorption system.

2.2.1 Porous properties

Nitrogen (N₂) adsorption is a very popular and standard procedure to determine the porous structure of adsorbents. N₂ adsorption/desorption isotherm is measured to understand the porous properties and also hysteresis behaviour of the adsorbent [43–46]. Nitrogen (N₂) adsorption isotherms are measured at 77 K using volumetric method [43,45,47,48]. The isotherm data is then analyse using BET (Brunauer-Emmett-Teller) method to determine the specific surface area [46–50]. The reported BET-surface area for activated carbon (AC) lies between 462–3045 m² g⁻¹ depending on the type and manufacturer as can be seen from Table 2.1.

The pore volume and size distribution analyses are conducted using the non-local density functional theory (NLDFT). The details of this theory is beyond the scope of this thesis and can be found elsewhere [46,48,50]. The NLDFT method is integrated into the analysis software to generate the pore size distribution of an adsorbent based on isotherm data. Numerous literature (Table 2.1) reported that the pore volume of commercially ACs

is typically in the range of $0.43\text{--}1.73\text{ cm}^3\text{ g}^{-1}$ with an average pore diameter of $\sim 4.0\text{ nm}$. It is found that until now commercially available Maxsorb III possesses the higher BET-surface area and pore volume, which attributed higher adsorption uptake of ethanol and CO_2 .

Fig. 2.4 describes the equilibrium uptake of ethanol and CO_2 onto various AC based adsorbent with respect to the pore volume of the adsorbent. It is observed that uptake increases with the increase of pore volume of the adsorbent. It is found that commercial AC Maxsorb III shows higher CO_2 and ethanol adsorption compared to any other ACs commercially available. Recently, Kil et al. [51] developed laboratory scale two ACs from phenol resin which possess higher pore volume than Maxsorb III, as a result shows higher ethanol uptake than Maxsorb III. However, there is no experimental data for CO_2 adsorption. An important point needs to mention that these phenol resin-derived ACs also a same trend (Fig. 2.4) as a function of pore volume.

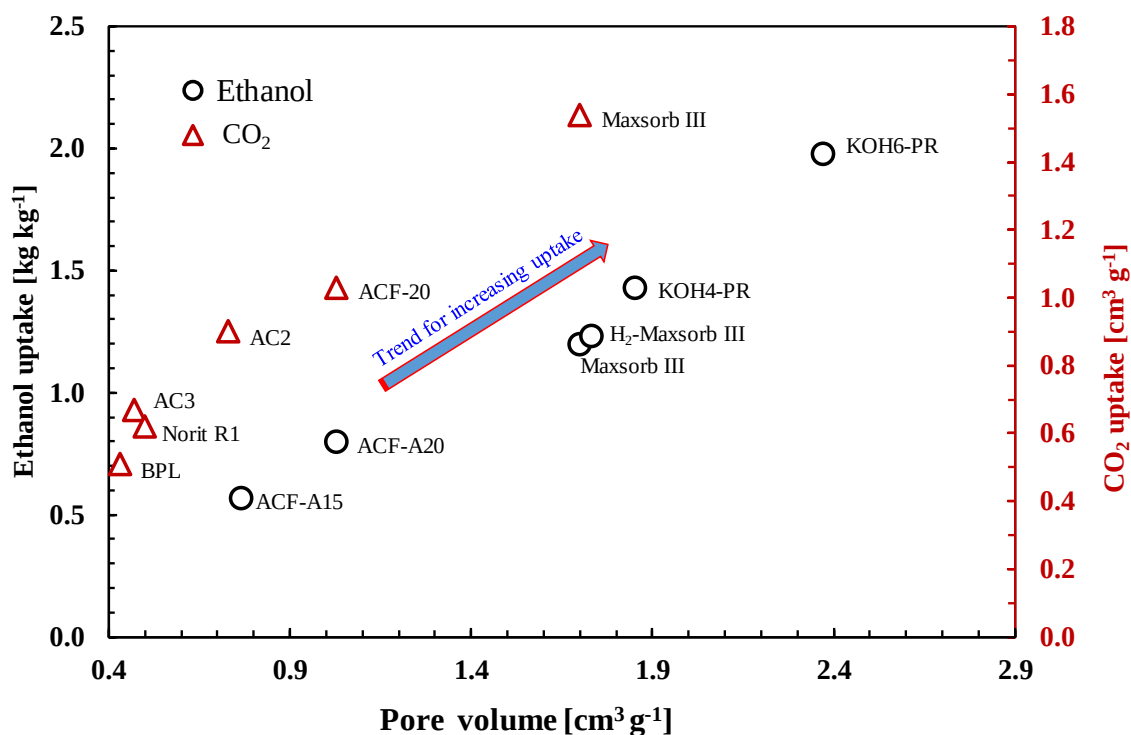


Fig. 2.4 Equilibrium uptake of ethanol and CO_2 adsorption onto various activated carbon based adsorbent as a function of pore volume [14–16,18,36,37,39,52].

2.2.2 Uptake and kinetics measurement techniques

In order to get the adsorption isotherm plot, the change in refrigerant mass adsorbed by the adsorbent is needed to measure. Volumetric and gravimetric are two best

extensively techniques used to measure the adsorption uptake. The volumetric method is known as constant volume variable pressure (CVVP) method. In this method, the uptake is predicted by measuring the pressure changes in a charging cell of refrigerant vapor at a constant temperature. At first, refrigerant charging cell is filled with the refrigerant vapor at a certain pressure, and it is then connected to adsorption cell unit containing the adsorbent. The charging cell pressure changes as the adsorption take places. This method has been used by many researchers [11,17,36,43]. However, gravimetric technique measures the adsorbent weight directly during the adsorption process in order to determine the uptake variation [14–16,53–57]. Highly sophisticated measuring systems are required for this method. Usually, the thermo-gravimetric analyzer (TGA) having high precision magnetic or micro-balance is used for the direct measurement of adsorption uptake. Therefore, data obtained from this method very precious and system allows using a small amount of sample mass. Both of the above methods use highly sophisticated instrumentation and automatic control system. However, these are very expensive.

The instantaneous behavior of adsorption uptake, known as adsorption kinetics, is equally important as the determination of equilibrium adsorption isotherm. Adsorption kinetics implies the measurement of uptake as a function of time during the adsorption and desorption process. Therefore, the measurement technique should be highly sensitive to the mass variation to obtain the kinetics curve. Both above mentioned techniques can be used for the kinetics measurement. However, gravimetric (TGA) technique provides more accurate time-dependent data compared to CVVP, since the TGA measures the sample weight directly.

2.2.3 Adsorption isotherms and kinetics

The plot of adsorption uptake of any adsorbent/adsorbate pair in a pressure-uptake plane is known as isotherm. Isotherm is essential fundamental characteristics of any adsorbent/adsorbate pair. Freundlich [29,58] and Langmuir [59,60] made the leading efforts to represent the adsorption uptake as a function of pressure and temperature. In the Langmuir model, a monolayer coverage of adsorbate molecules on adsorbent surface is assumed. To relate the amount of adsorbate to its partial pressure at the particular temperature an equation is derived. This model can be employed to represent type I adsorption isotherm. An equation is derived by Brunauer et al. [61] for multi-layer adsorption process and can be denoted type I and II adsorption isotherms. For describing

high pressure adsorption isotherms namely CO₂ adsorption onto carbon based adsorbents, Dubinin-Astakhov (D-A) equation [29,62,63] has been widely used. However, numerous challenges have been made for low pressure adsorption isotherms like ethanol on activated carbon [14–16], water on silica gel [43,64] and zeolite [65]. Tóth [66] presented single equation to represent different types (type I, II, III and V) of adsorption isotherms by modifying the constants in the equation. Therefore, Tóth equation suitably defines the isotherms for both high [17,36,67] and low pressure equilibrium adsorption isotherm [11].

Various mathematical models are employed to describe the dynamic adsorption behaviour of activated carbon/ethanol and CO₂ pair. Linear driving force (LDF) and Fickian diffusion (FD) are prevalent models to describe the adsorption kinetics of activated carbon based adsorbent/ethanol and CO₂ pair [14,16,18,53,54]. LDF equation has been used by many researchers in their simulation studies. The Fickian diffusion (FD) model provides a logical expression for microscopic adsorption uptake. El-Sharkawy [68] found that there is a significant difference between the uptakes predicted by FD and LDF models and proposed time and temperature dependent corrections to the LDF model.

2.2.4 Thermal properties

Thermal conductivity and specific heat capacity of the adsorbent and heat of adsorption of adsorbent/refrigerant pair are the critical thermal parameters affecting the design of an adsorption system. The thermal conductivity of the adsorbent influences the thermal diffusivity through adsorber whereas the isosteric heat of adsorption represents the strength of adsorbate/adsorbent interaction. Specific heat capacity is also one of the important parameters for assessment, calculation, and design of the thermal system.

2.2.4.1 Thermal conductivity of ACs

Adsorbents employed for adsorption heat pump systems are mainly powder and granular form. As a result, adsorbent particles are loosely packed in the bed. Consequently, their thermal conductivity is very low which hinders the widespread use of adsorption technologies. The thermal conductivity of AC is typically provided by the manufacturer or sometimes measured by the researchers. It is usually measured by steady state, transient or laser flash method. Table 2.3 represents the thermal conductivity of some commonly used AC reported in the literature. It can be seen that thermal conductivity of AC is very low and depends on the type.

Table 2.3 Thermal conductivity of some commonly used AC reported in the literature.

Sample	Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	Reference
Parent adsorbent (powder or granular form)		
Maxsorb III (AC)	0.066	[46]
Granular AC from Chemviron (80-100) mesh	0.23	[69]
Coconut shell-AC (type XY-20)	0.36	[70]

2.2.4.2 Isosteric heat of adsorption

The determination of Q_{st} is crucial for kinetic studies and performance evaluation of adsorption system. The heat released during the adsorption is partially adsorbed by the adsorbent, which causes a rise in adsorbent temperature and thus influences the rate of adsorption. Q_{st} depends on adsorbent/adsorbate pair. For example, Q_{st} of Maxsorb III/ethanol pair is different from Maxsorb III/ CO_2 pair, although adsorbent is same. The isosteric heat of adsorption at constant uptake is estimated from adsorption equilibrium data using Clausius-Clapeyron equation which is given by:

$$\frac{-Q_{st(CC)}M}{R} = \frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)} \quad (2.1)$$

Where, Q_{st} denotes the isosteric heat of adsorption [kJ kg^{-1}], which is a negative quantity because of the exothermic process, R represents the universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], M is molar constant [g mol^{-1}].

The heat of adsorption is derived from adsorption isotherm, and hence, its numerical value and dependency on uptake differ with the type of isotherm used. Langmuir and Tóth isotherm relation treats isosteric heat of adsorption as constant whereas according to D-A isosteric heat of adsorption has uptake and temperature dependency. Therefore, heats of adsorption vary from isotherm model to model. The heat of adsorption derived from D-A equation can be represented by equation (2.2) [15,71–73]. This equation usually uses for adsorbent/ethanol pair.

$$-Q_{st} = RT^2 \frac{\partial}{\partial T} \ln(P_s) + E \left\{ -\ln \left(\frac{W}{W_0} \right) \right\}^{\frac{1}{n}} \quad (2.2)$$

The isosteric heat of adsorption derived from the modified D–A equation for adsorption isotherm of adsorbent/CO₂ (high pressure adsorbate) pairs is expressed by equation (2.3) [17,29,38].

$$Q_{CC,m(D-A)} = RT^2 \frac{\partial \ln P_s}{\partial T} + A + \frac{\alpha}{n} TE^n A^{1-n} \quad (2.3)$$

$$\text{Where, } RT^2 \frac{\partial \ln P_s}{\partial T} = kRT \text{ for } T > T_C$$

Chakraborty et al. [71] modified the equation (2.3) by introducing an extra term, which accounts heat of adsorbed mass with respect to pressure and temperature changes during the adsorption process of high pressure gas, and the modified equation is given by the equation (2.4).

$$Q_{Chak,m(D-A)} = kRT + A + \frac{\alpha}{n} TE^n A^{1-n} + Tv_g \left(\frac{\partial P}{\partial T} \right) \quad (2.4)$$

Table 2.4 summarized the average heat of adsorption for activated carbon/ethanol and activated carbon/CO₂ pairs. Since adsorbent/adsorbate is different, so, Q_{st} values are different. It is found from the literature study that Q_{st} for AC/ethanol pairs varies between 900 to 1100 kJ kg⁻¹ whereas 15 to 25 kJ mol⁻¹ are for AC/CO₂ pairs.

Table 2.4 Average value of the heat of adsorption (Q_{st}) of AC/ethanol and AC/CO₂ pairs.

Adsorbent/adsorbate pair	Average heat of adsorption, Q_{st}	Reference
Ethanol/ KOH4-PR	1070 kJ kg ⁻¹	[14]
Ethanol/ KOH6-PR	995 kJ kg ⁻¹	[14]
Ethanol/Maxsorb III	1002 kJ kg ⁻¹	[15]
Ethanol/H ₂ -Maxsorb III	963 kJ kg ⁻¹	[15]
Ethanol/KOH-H ₂ -Maxsorb III	926 kJ kg ⁻¹	[15]
Ethanol/ACF (A-20)	1050 kJ kg ⁻¹	[37]
Ethanol/ACF (A-15)	1050 kJ kg ⁻¹	[37]
CO ₂ /Maxsorb III	19.30 kJ mol ⁻¹	[18]
CO ₂ /Maxsorb III	20.37 kJ mol ⁻¹	[17]
CO ₂ /CSAC	16.44 kJ mol ⁻¹	[38]
CO ₂ /ACF (A-20)	19.23 kJ mol ⁻¹	[17]
CO ₂ /AC1	15.51 kJ mol ⁻¹	[39]
CO ₂ /AC2	16.27 kJ mol ⁻¹	[39]
CO ₂ /AC3	16.53 kJ mol ⁻¹	[39]
CO ₂ /BPL	25.7 kJ mol ⁻¹	[36,39]
CO ₂ /Norit R1 Extra	22.0 kJ mol ⁻¹	[36,39]
CO ₂ /Norit Darco	20.82 kJ mol ⁻¹	[39]

2.2.4.3 Specific heat capacity of ACs

Specific heat capacity (C_p) as a fundamental thermal property is one of the main parameters for assessment, calculation, and design of the thermal system. It is defined as the required heat per unit mass of material when raising the temperature of 1 K and usually, it is a function of temperature. The changing C_p value with temperature depends on the material types. Activated carbon has been extensively employed in adsorption heat pump cycle. Activated carbons are usually microporous. The specific heat capacity of such porous materials is an essential parameter in adsorption cycle simulation and system design. Therefore, one needs to determine the specific heat capacity of the adsorbents for application to AHP systems.

Uddin et al. [74] experimentally measured the specific heat capacity of widely used various activated carbons using a heat flux type differential scanning calorimeter (DSC).

The experiment was conducted in N₂ atmosphere at temperatures ranging from 30 to 150°C. Table 2.5 shows the C_p of widely used ACs in the operating temperature of AHP cycle. It is observed that C_p varies between 0.7 to 1.2 J g⁻¹ K⁻¹ and KOH-H₂-Maxsorb III shows highest C_p whereas KOH6-PR possess lowest C_p .

Table 2.5 Specific heat capacity of ACs [74].

Temperature [°C]	Specific heat capacity (C_p) [J g ⁻¹ K ⁻¹]			
	Maxsorb III	H ₂ -Maxsorb III	KOH-H ₂ -Maxsorb III	KOH6-PR
30	0.844	0.949	1.06	0.751
50	0.876	0.969	1.098	0.756
70	0.914	0.994	1.135	0.768
80	0.931	1.007	1.164	0.774
90	0.95	1.023	1.184	0.783
100	0.969	1.035	1.20	0.789

2.3 Activated carbon based adsorption cooling systems

Many researchers have been studied a number of activated carbon based adsorption cooling systems using various environment friendly refrigerants, like ethanol, methanol, and CO₂. This study has been presented experimental, data analysis using various theoretical model, and performance investigation of different adsorption cooling systems with activated carbon as the adsorbent.

2.3.1 Activated carbon/ethanol pair

The performance of the cooling system with activated carbon as adsorbent and ethanol as a refrigerant was studied by many researchers. El-Sharkawy et al. [75] experimentally studied ethanol adsorption onto highly porous activated carbon Maxsorb III using a thermogravimetric analyzer (TGA) at various adsorption temperatures. An experimental result showed that maximum uptake of Maxsorb III/ethanol was 1.2 kg kg⁻¹. This pair showed specific cooling effect (SCE) as high as 420 kJ per kg at the evaporator temperature of 7°C along with heat source and coolant temperatures of 80 and 30°C,

respectively. The proposed pair seems to be attractive for solar adsorption cooling applications due to high adsorption uptake of ethanol onto Maxsorb III and low adsorption temperature of the pair, which is below 100°C. El-Sharkawy et al. [76] investigated the adsorption equilibrium of Unitika activated carbon fiber (ACF) of types (A-20)/ethanol and (A-15)/ethanol pairs. Dubinin–Radushkevich (D–R) equation was used to correlate the measured data. They found ACF (A-20)/ethanol pair had higher adsorption capacity than ACF (A-15)/ethanol pair. They also observed that adsorption rate per unit volume of adsorber increased with increasing bed apparent density, which may lead to the design a compact adsorption system. Saha et al. [77,78] modelled a two bed adsorption cooling system using ACF/ethanol pair. This innovative system utilized effectively low-temperature waste heat temperature between 60 and 95°C along with a heat sink at 30°C. Optimum cooling capacity values were obtained for a cycle time at 600 s with a fixed pre-heating or pre-cooling cycle time. Optimum switching time for the chiller was between 30 and 50 s. They found that COP reached about 0.6 with a cycle time of 600–700 s.

2.3.2 Activated carbon/methanol pair

Zhao et al. [79] presented a mechanical and experimental study on freeze proof solar powered adsorption cooling tube using activated carbon/methanol pair. It was found that the maximum adsorbent bed and evaporation temperature were 110°C and –4°C, respectively. The cooling capacity of the freeze proof solar cooling tube was about 87–99 kJ; and the COP was about 0.11. El-Sharkawy et al. [80] studied the adsorption of methanol onto carbon based adsorbents. The study presented the methanol adsorption isotherms onto two sample namely, Maxsorb III and Tsurumi activated charcoal. Dubinin Raduskevich (D-R) equation was employed to fit the measured data and to draw the pressure–temperature–uptake (P-T-W) plot for both pairs. Results showed adsorption uptake of Maxsorb III/methanol pair was about 72% higher compared to activated charcoal/methanol pair. The maximum COP was 0.78 with Maxsorb III/methanol at desorption temperature of 90°C. This study revealed that Maxsorb III/methanol pair was superior among other carbon-based pairs for both of air-conditioning and ice-making applications. Wang et al. [81] proposed a hybrid system of activated carbon/methanol based solar powered water heater and refrigerator. It was competent of heating 60 kg of water to about 90°C and producing 10 kg of ice per day with a 2 m² solar collector. Luo et al. [82] established activated carbon/methanol adsorption pair for a solar adsorption ice maker application.

The main feature was utilization of a water cooled condenser and removing all valves in the refrigerant circuit except the one that was necessary for refrigerant charging. Compared with an air-cooled condenser, the water-cooled condenser run more effectively. Results showed that the COP of the solar icemaker is about 0.083–0.127. The daily ice production varied within the range of 3.2–6.5 kg m⁻². Pons et al. [83] accomplished an experiment with activated carbon and methanol based solar adsorption refrigeration system. The system was loaded with 130 kg of activated carbon and produced around 30–35 kg of ice on sunny days. The system used flat-plate collector having an exposed area of 6m². This study reported that the system COP was about 0.12.

2.3.3 Activated carbon/carbon dioxide (CO₂) pair

Saha et al. [17] studied adsorption isotherms of CO₂ onto highly porous activated carbon fiber (ACF) of type A-20 and activated carbon powder of type Maxsorb III for wide temperatures and pressure range. Authors found that the Tóth and modified Dubinin-Astakhov (D-A) models were well matched with the experimental data within ±5% RMSD compared to Langmuir and D-A equations. It was found that the maximum uptake of ACF (A-20)/CO₂ pair was 1 kg kg⁻¹ whereas 1.7 kg of CO₂ per kg of Maxsorb III, which was 1.7 times higher than that of A-20. The average heats of adsorption of CO₂ in Maxsorb III and ACF (A-20) were found to be 20.37 and 19.23 kJ mol⁻¹, respectively. Jribi et al. [84] studied activated carbon (Maxsorb and ACF-A10)/CO₂ based adsorption cooling cycles using pressure–temperature–uptake (P–T–W) diagram. The SCE and the COP of these two cooling systems were simulated for various temperatures. It was found that Maxsorb/CO₂ couple showed higher cooling capacity and COP. The maximum COPs of Maxsorb/CO₂ and ACF (A10)-CO₂ based cooling systems were found 0.15 and 0.083, respectively. The main feature of this cooling cycle was to utilize low temperature waste heat or solar energy. Jribi et al. [85] introduced a transient mathematical model for a 4-bed adsorption chiller using Maxsorb III/CO₂ pair for different heating, cooling and chilled water inlet temperatures. For cooling water inlet temperature of 27°C, the optimal desorption pressure and the optimal adsorption/desorption time were found to be 7.9 MPa and 575 s, respectively. The system was able to produce 1.72 kW of cooling power at driving heat source temperature of 85°C. The maximum COP was found to be 0.1. Shen et al. [86] studied adsorption equilibria experimentally and kinetics of activated carbon in beads form/CO₂ pair. The CO₂ adsorption uptake was measured at various temperatures and

pressures. The highest adsorption capacity was 0.0844 g g^{-1} at 30°C and 100 kPa . The isosteric heat was determined to be $23.17 \text{ kJ mol}^{-1}$. Zhong et al. [87] investigated the performance of CO_2 as a refrigerant in adsorption refrigeration systems using several types of carbon as adsorbents.

2.3.4 AC based consolidated composites

A fundamental problem with the activated carbon (AC) powder as an adsorbent used in adsorption cooling systems is their very low thermal conductivity. In order to complete a thermodynamic cycle, adsorbent must be heated during the desorption process and then cooled down in adsorption process and finally returns to ambient temperature. For completing each adsorption cycle, a specific quantity of heat is needed for pumping between two processes. In order to improve the performance of adsorption cooling systems, it must be physically small and therefore the time per adsorption cycle must be small. This, in turn, entails high rates of heat transfer in and out of the adsorber bed. Therefore, using of the consolidated composite adsorbent with high thermal conductivity is one of the methods in order to increase adsorption system performance. Recently, many notable researchers intensely focused on consolidated composite adsorbents to enhance the heat transfer into adsorber/desorber bed. As a result, it improves the adsorption cooling system performance. Researchers have been achieved significant improvement of thermal conductivity of adsorbents using consolidated composite materials as adsorbents. Following is some representative examples: Zhao et al. [88] studied on consolidated carbon for refrigeration application. Six samples of three types of adsorbents (consolidated AC with expanded natural graphite treated with sulfuric acid (ENG-TSA), consolidated AC with expanded natural graphite (ENG) and granular AC) with different density and different grain size were produced and compared. The making process of consolidated composite AC is shown in Fig. 2.5. The thermal conductivity was measured by the NETZSCH LFA 447 NanoFlash using the laser flash measuring method Results show that with the addition of ENG-TSA, the thermal conductivity of composite AC increases significantly. The thermal conductivity of consolidated AC with ENG-TSA is $7.45 \text{ W m}^{-1} \text{ K}^{-1}$ at the density of 400 kg m^{-3} , which is 3 times as high as that of consolidated AC with ENG at the density of 400 kg m^{-3} and is 45 times higher than that of granular AC. The samples with AC of small grain size have much higher thermal conductivity. The permeability of consolidated AC with ENG-TSA is between $5.00 \times 10^{-12} \text{ m}^2$ and $1.00 \times 10^{-12} \text{ m}^2$.

12 m^2 when the density is ranged between 350 kg m^{-3} and 450 kg m^{-3} . Cacciola et al. [89] developed brick shaped adsorbent materials based on activated carbons and PTFE (poly-tetra-fluorethylene) as a binder. They reported that the adsorption capacity of methanol onto the developed adsorbents is higher than 40% and the thermal conductivity ranging from 0.13 to $0.20 \text{ W m}^{-1} \text{ K}^{-1}$. Jin et al. [70] measured thermal conductivity and permeability of granular activated carbon (AC), consolidated AC with a chemical binder and consolidated AC with expanded natural graphite. The authors reported that thermal conductivity of granular activated carbon and consolidated activated carbon with chemical binder are about $0.36 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.4 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The thermal conductivity was $2.08 \text{ W m}^{-1} \text{ K}^{-1}$ to $2.61 \text{ W m}^{-1} \text{ K}^{-1}$, however, its permeability is lower than that of the granular AC and consolidated AC with a chemical binder.

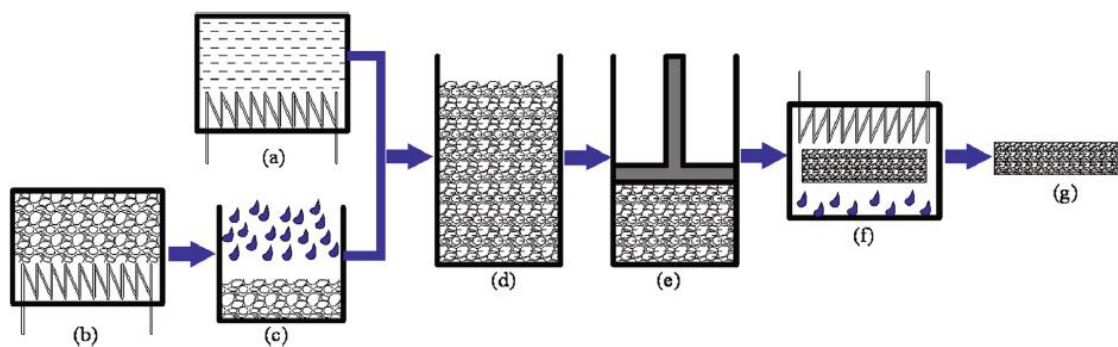


Fig. 2.5 Manufacture processes of consolidated composite AC [88].

(a) drying process of granular ENG-TSA or ENG, (b) drying process of granular AC, (c) mixture of granular AC and water, (d) the composite adsorbent of AC, ENG-TSA or ENG, and water, (e) compressing process of composite adsorbent, (f) drying process of the consolidated adsorbent, (g) the consolidated composite adsorbent samples for test.

Tamainot-Telto et al. [90] measured the thermos-physical properties of two types of monolithic activated carbons. The authors reported that the thermal conductivity of the tested samples was $0.44 \text{ W m}^{-1} \text{ K}^{-1}$ and the adsorption capacity for ammonia was 0.36 kg kg^{-1} . Wang et al. [91] developed composites which were combinations of activated carbon and expanded natural graphite. They found thermal conductivity and permeability were $2.47 \text{ W m}^{-1} \text{ K}^{-1}$ and $4.378 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively. Wang et al. [69] developed consolidated composite activated carbon (AC) with a host matrix of expanded natural graphite treated with sulfuric acid (ENG-TSA). Fig. 2.6 shows the photograph of developed adsorbents. The authors reported that the highest effective thermal conductivity

of consolidated composite AC was $34.2 \text{ W m}^{-1} \text{ K}^{-1}$ which was 150 times higher than conventional granular activated carbon.

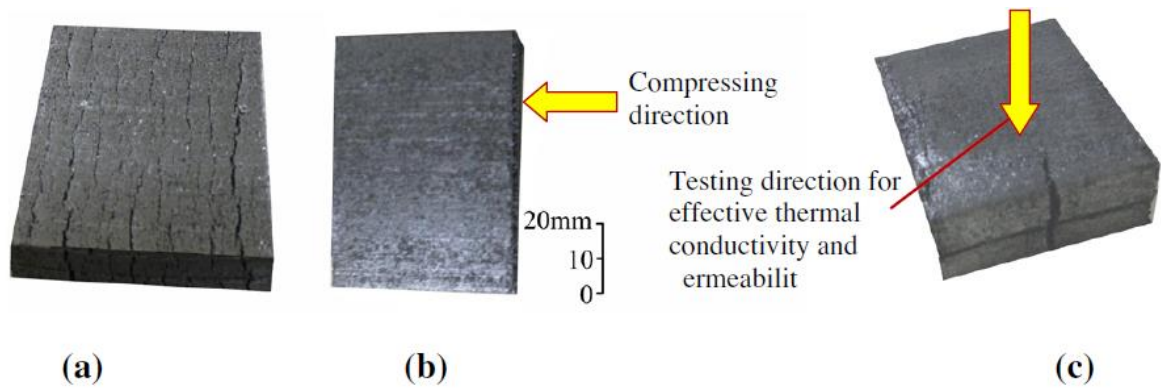


Fig. 2.6 Consolidated composite adsorbents, (a) density of 249 kgm^{-3} with cracks, (b) density of 388 kgm^{-3} without cracks, (c) density of 448 kgm^{-3} with cracks [69].

2.4 Scope of this thesis

Among the various adsorbents, activated carbons (AC) are receiving continuous attention owing to high porosity and hence high adsorption uptake of refrigerant vapor which plays a significant role for the performance improvement of AHP systems. The literature review indicated that so far commercially available widely used AC is Maxsorb III. It possesses the surface area and pore volume $3000 \text{ m}^2 \text{ g}^{-1}$ and $1.7 \text{ cm}^3 \text{ g}^{-1}$, respectively. Although its surface is very high, the adsorption uptake of ethanol and CO_2 is not as high as expected due to its quite low pore volume. The maximum adsorption uptake of ethanol and CO_2 are 1.2 kg kg^{-1} and $1.54 \text{ cm}^3 \text{ g}^{-1}$, respectively. Moreover, the commercially available most of ACs are employed for AHP application prepared from non-renewable precursor materials such as petroleum, coal, coke or pitch and those are very expensive. Because of the renewability and relatively low price, biomass, such as waste palm trunk, and waste wood (mangrove), is one of the suitable candidates as raw materials of ACs. Furthermore, in case of the AHP applications, a presence of ashes in the biomass-derived ACs is considered not to be a severe problem, unlike the electrochemical applications. Regardless of several studies on preparation of biomass-derived ACs, however, fewer studies using the biomass-derived ACs for AHP applications have been reported. In addition, highest pore volume biomass-derived ACs is $1.73 \text{ cm}^3 \text{ g}^{-1}$ so far (Table 2.2). Consequently, the author is going to study the biomass-derived ACs for AHP systems.

In addition to that if pore volume of AC increases the adsorption uptake of both ethanol and CO₂ refrigerants increase as can be seen from Fig. 2.4. Hence, there is a scope to enhance the adsorption uptake by increasing the pore volume of ACs. In this study, the author has been tried to prepare large pore volume and high surface ACs with suitable pore width by controlling activation conditions using waste palm trunk and mangrove as precursors. The synthesized all ACs have been characterized through N₂ adsorption/desorption, porous properties, particle size distribution and thermal conductivity. Feasibility of the prepared biomass-derived ACs as an adsorbent for the ethanol and CO₂ based AHP system will be investigated. Furthermore, equilibrium performance (SCE and COP) will be investigated of the selected biomass-derived ACs/ethanol and CO₂ pairs and compared to other ACs.

Additionally, all the prior reports on activated carbon/ethanol and CO₂ pairs pointed towards adsorption characteristics and effect of operational parameters on system performance. There are very few studies focused on thermal diffusivity and conductivity improvement of AC by making composite adsorbents. Still, it is a virgin and potential research area. Moreover, ACs usually in powder or granular form. Therefore, it is urgently necessary to enhance the thermal conductivity of AC, which in turns increases the heat transfer into the adsorber. As a result, the system performance will increase and also possible to make compact AC carbon based AHP system. Hence, this study will provide a detailed account of not only the synthesis of composite but also the fundamental characterization of composites. AC composite will be prepared using different kinds of additives. Role of these additives material in AC composites will be discussed in details. Finally, the investigation of adsorption characteristics of ethanol and CO₂ onto developed composites will be presented. Furthermore, equilibrium thermodynamic performance such as SCE and COP will be presented and compared to other ACs.

From the literature review, it is evident that the consolidated composite adsorbents have attracted considerable attention as next generation adsorbents in AHP application because of their some salient features, such as improved uptake to volume ratio and high thermal conductivity. Notable researchers have been employed a number of binders such as expanded graphite [88], polyvinyl alcohol (PVA) [46], polytetrafluoroethylene (PTFE) [89], polyvinylpyrrolidone (PVP) [92] to synthesis composites with good thermal conductivity. However, the punitive reality of using such synthetic polymers type binders is the reduction in the adsorption capacity due to poor affinity for refrigerant vapor

[70,89,93]. Therefore, it is required to find appropriate binders that not only suitable for stable consolidate composites but improve thermal conductivity with efficient sorption capabilities. To address these issues, a polymerized ionic liquid (IL), which works as an adsorbent, has been explored as a potential binder in making activated carbon based composites. One of the promising application of the polymerized ionic liquid is in the CO₂ capture. According to Shahrom et al. [94], the CO₂ sorption capacity increases in polymerized ionic liquids. Authors studied various polymerized amino acid-based ionic liquids (PAAILs) to enhance the adsorbing CO₂. The results showed that PAAILs are capable of capturing CO₂ more than other ionic liquids. Various types of amine-functionalized poly(ionic liquid) adsorbents were studied for CO₂ capturing and authors found amino acids showed high adsorption capacity of CO₂ [95,96]. From the above perspective, for the first time in this research field, the author is going to extensive study on the utilization of polymerized IL as a binder in the synthesis of activated carbon based composites for AHP.

Consequently, this thesis provides a detailed synthesis and characterization studies on next generation adsorbents such as biomass-derived high surface area and pore volume ACs and consolidated composites for AHP applications. The research outcome of this study will play the significant role in making high performance AHP with compact size.

2.5 Approaches to this thesis

This section provides the conceptual approaches regarding to reach the scopes as discussed in the previous sections. To improve the performance of AHP system and compact size, there are several approaches such proper system design, improvement of effective adsorption uptake, adsorption/desorption kinetics and thermal conductivity (Fig. 2.7). It is known that effective adsorption uptake, adsorption/desorption kinetics and thermal conductivity are related to adsorbent properties. In this thesis, the author has been focused the synthesis of adsorbent material for the improvement of effective adsorption uptake and thermal conductivity.

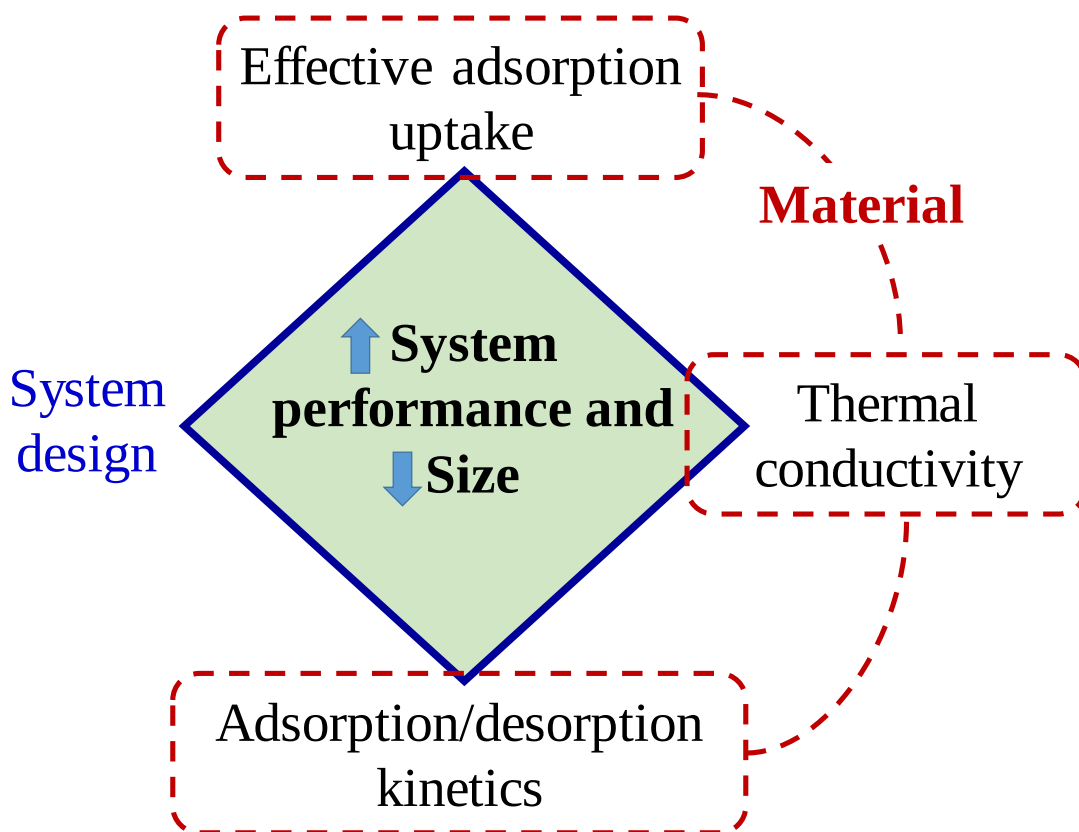


Fig. 2.7 Parameters affect the system performance and compactness.

2.5.1 Effective uptake improvement approach

Large pore volume and high surface area ACs have been prepared from biomasses namely waste palm trunk and mangrove wood by carbonization (500 and 600°C) followed by KOH activation (600-900°C and 4-6 times KOH). The effective uptake is defined as the difference between the maximum and minimum uptake (Fig. 2.8) at the particular operating condition. Fig. 2.8 shows the representation of effective and obtaining highly porous ACs from biomasses for AHP applications. Since the highest uptake of Maxsorb III is 1.2 kg kg^{-1} , therefore, to find the alternative and new sources of precursors is essential to prepare ACs. Solid lines (Fig. 2.8) comprised rectangular area represents the effective uptake of Maxsorb III/ethanol pair whereas dotted blue comprised rectangular area shows the expected effective uptake from biomass-derived ACs/ethanol pair at particular AHP cycle.

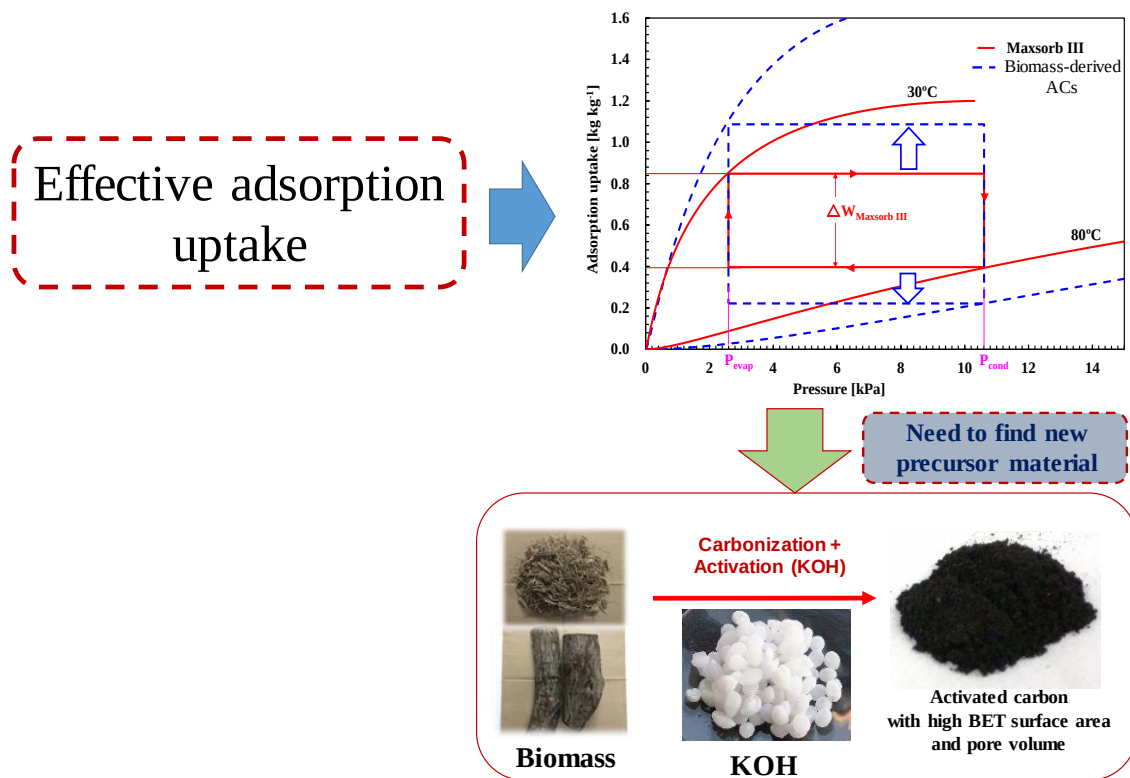


Fig. 2.8 Schematic representation of effective uptake definition and way to obtain large pore volume with high surface area ACs.

2.5.2 Thermal conductivity improvement approach

The main drawbacks of the AC/ethanol or AC/CO₂ based system are large geometry and low SCE and COP which hinders the wide-spread dissemination of the system [97–99]. These drawbacks are generally related to the low packing density and low thermal conductivity of AC that is usually either powder or granular form [100]. The bulk density of AC powder is very low which is about 170 kg m^{-3} , and it can be compressed up to 290 kg m^{-3} at higher pressure [46,48,101]. Furthermore, thermal conductivity of AC varies from 0.044 to $0.36 \text{ W m}^{-1} \text{ K}^{-1}$ [46,69,70,102], which is also very poor value. Consequently, it is necessary to enhance the conductivity of AC as well packing density for performance improvement and compactness of AHP systems. The thermal conductivity enhancement of AC powder could be done by adding thermal conductivity enhancer and compressing the mixing AC composite material (Fig. 2.9). AC composite will be prepared using additives such as expanded graphite (EG)/graphene nanoplatelets (GNPs) and binder. Therefore, additives material can create thermal network into AC composite as can be seen in Fig. 2.9.

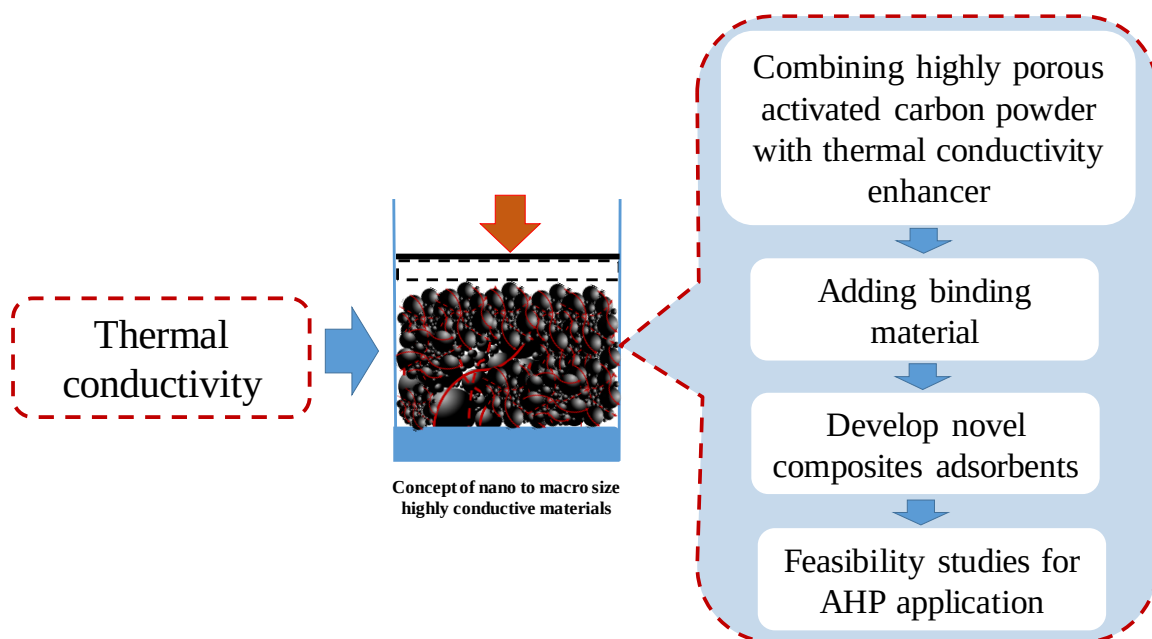


Fig. 2.9 Schematic drawing for creating a thermal network using additives.

Chapter 3

Development of adsorbent material

The primary concern of promising adsorbent material that must be fulfilled are high porous properties, high thermal conductivity, high adsorption uptake with no hysteresis, thermally stable, low costs and renewable. In this regard, this chapter presents the synthesis and characterization of various kinds of AC based adsorbents: i) waste biomass-derived extremely porous ACs through the optimization of the experimental conditions; ii) composite adsorbents using expanded graphite (EG) and graphene nanoplatelets (GNPs) as a thermal conductivity enhancer; iii) synthesis of polymerized ionic liquid (PIL) and composite using PIL as a binder. The N₂ adsorption/desorption experiment at 77 K and thermal conductivity measurement are conducted for estimating the porous properties and thermal conductivity of all synthesized adsorbent, respectively. Surface morphology of all synthesized biomass-derived ACs is also investigated using scanning electron microscopy (SEM).

3.1 Introduction

Adsorption heat pump (AHP) systems have gained considerable attention due to use of environmentally friendly working fluid and can be driven low-temperature (< 100°C) waste heat [15,16,76,97,103,104]. Activated carbon (AC) and AC based adsorbents are very promising adsorbent for application of the adsorption heat pumps due to its high porous properties and high adsorption affinity towards the many gasses such as ethanol, CO₂, methanol. A number of notable researchers mentioned that carbon-based adsorbent with the high surface area having microsize pores, and large pore volume is potential for AHP applications. However, these widely used AC is expensive, made from non-renewable precursor material such as coke and petroleum residue [31,105,106]. ACs can be synthesized from renewable resources in various ways. Recently, numerous researchers have been prepared AC from a different source of waste biomasses as it is renewable and cheap [107–110]. Yang et al. [108] prepared AC from coconut shell using activating agents such as steam, CO₂ and a mixture of steam-CO₂ with microwave heating. Results showed that BET surface area of AC irrespective of the activation agent resulted

in surface area in excess of $2000 \text{ m}^2 \text{ g}^{-1}$. Kyzas et al. [109] investigated the use of AC after pyrolysis of waste potato peels. The activation agent was phosphoric acid, while three different carbons were prepared based on the different activation temperatures (400, 600, 800°C). The highest achievable surface area was $1041.43 \text{ m}^2 \text{ g}^{-1}$. Hao et al. [111] synthesized ACs from hydrothermally carbonized waste biomass for CO_2 capture from flue gas. Mahamad et al. [112] prepared AC from the pyrolysis (500°C , 1 h) of pineapple waste biomass (leaves, stem, crown) impregnated with ZnCl_2 for dye removal. Resulting AC showed the surface area as high as $914.67 \text{ m}^2 \text{ g}^{-1}$. Nor'Azizi Bin Othman [113] synthesized the activated carbons using KOH and steam activation from waste palm trunk (WPT). Other related articles can be found elsewhere [114–116].

Furthermore, usually, AC is powder or granular form that possesses low thermal conductivity, loosely packed as a result low volumetric cooling/refrigeration capacity and the system becomes bulky. Therefore, adsorption characteristics and thermal conductivity are two vital properties that are needed to improve for making AHP system more promising. Since AC possesses very high adsorption uptake compared to other adsorbents. Therefore, it is necessary to enhance heat transfer properties of AC for more widespread use. Consequently, heat intensification of AC could be done by making consolidated composite adsorbents using various additives material during synthesis which are attracted much attention of many researchers in recent years. Following are some representative examples. Cacciola et al. [89] developed brick shaped adsorbent materials based on activated carbons and PTFE (poly-tetra-fluoro-ethylene) as a binder. They reported that the adsorption capacity of methanol onto the developed adsorbents is higher than 40% and the thermal conductivity ranging from 0.13 to $0.20 \text{ W m}^{-1} \text{ K}^{-1}$. Jin et al. [117] tested thermal conductivity and permeability of granular activated carbon (AC), consolidated AC with a chemical binder and consolidated AC with expanded natural graphite. The authors reported that thermal conductivity of granular activated carbon and consolidated activated carbon with chemical binder were about $0.36 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.4 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The thermal conductivity of consolidated activated carbon with expanded natural graphite was ranging from $2.08 \text{ W m}^{-1} \text{ K}^{-1}$ to $2.61 \text{ W m}^{-1} \text{ K}^{-1}$, however, its permeability was lower than that of the granular AC and consolidated AC with a chemical binder. Tamainot-Telto et al. [100] measured the thermophysical properties of two types of monolithic activated carbons. The authors reported that the thermal conductivity of the tested samples was 0.44

$\text{W m}^{-1} \text{K}^{-1}$ and the adsorption capacity for ammonia was 0.36 kg kg^{-1} . Wang et al. [91] developed composite adsorbents which were combinations of activated carbon and expanded natural graphite. Thermal conductivity and permeability were experimentally investigated. They reported that the best values of measured thermal conductivity and permeability were $2.47 \text{ W m}^{-1} \text{K}^{-1}$ and $4.378 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$, respectively. Wang et al. [69] developed consolidated composite activated carbon (AC) with a host matrix of expanded natural graphite treated with sulfuric acid (ENG-TSA). The authors reported that the highest effective thermal conductivity of consolidated composite AC was $34.2 \text{ W m}^{-1} \text{K}^{-1}$ which was 150 times higher than ordinary granular activated carbon. Zheng et al. [118] proposed composite desiccant adsorbent that comprises silica gel silica gel with expanded natural graphite treated with sulfuric acid (ENG-TSA) as a host matrix. It was reported that the highest thermal conductivity of consolidated composite adsorbents increased more than 270 times as compared to that of pure silica gel. Other related research work can be found elsewhere [119–123].

Regardless of various studies on synthesis of biomass-derived AC, fewer researchers have been achieved to prepare AC with the very high surface area from biomasses. In addition, there are no significant studies, which focus on, biomass-derived AC for AHP applications. Consequently, firstly this chapter presents the optimized experimental conditions of synthesis process of AC to obtain very high surface area and pore volume. Secondly, this chapter includes synthesis of carbon based composite adsorbents using polyvinyl alcohol (PVA) as a binder and thermal conductivity enhancer such as expanded graphite (EG) and graphene nanoplatelets (GNPs). Thirdly, instead of using PVA binder, polymer form of ionic liquid (PIL) named as vinyl benzyl trimethyl ammonium alanate, and its composites are synthesized for enhancing the adsorption uptake compared to traditional binder based composites. Porous properties from N_2 adsorption isotherms at 77K, thermal conductivity, and particle size distribution are investigated and discussed for all synthesized adsorbents in each section.

3.2 Synthesis and characterization biomass-derived functional ACs

Biomass is considered as one of the promising precursor materials for the synthesis of highly porous activated carbon (AC). Mainly, biomass can be a renewable and cheap source. Biomass-derived AC has extraordinary structures, such as heterogeneous texture

and its orientation, which do not usually appear in usual AC that is derived from coal and petroleum residues. Moreover, the presence of few percentages of ashes in the biomass-derived AC is accounted not to be a severe problem adsorption heat pump (AHP) applications, unlike the electrochemical applications. Therefore, this section presents the synthesis and characterization of biomass-derived functional ACs. Waste palm trunk (WPT) and mangrove (M) are employed for synthesis of biomass-derived ACs. There are many factors such as activation method; carbonization and activation temperature, activation agent type and amount affect the synthesis of highly porous ACs. Therefore, this study focuses on the influence of all these parameters to obtained optimized highly porous ACs from WPT and mangrove (M). N₂ adsorption/desorption isotherms, estimated porous properties, scanning electron microscopy (SEM) of developed are also presented.

3.2.1 Precursor materials

Properties of precursor material influences considerable the quality of the resulting AC. Although the chemical nature of the surface oxides and the surface area of the resulting products are determined by carbonization and activation method, the pore size distributions and the pore structure are mostly determined by the nature of the precursor material [113]. Low cost and renewable materials with high carbon and low ash content can be used as precursor materials. Waste palm trunk (WPT) and mangrove (M) are employed for making AC for AHP applications. Fig. 3.1 shows the pictorial view of two kinds of biomasses that are used for producing AC. From the photograph, it is seen that the WPT and M are structurally different from each other. As a result, both materials will be produced different surface area, surface morphology, micropore volume, and pore sized ACs at different carbonization and activation conditions, as expected. The elemental compositions of WPT and mangrove are shown in Table 3.1. The carbon content of raw WPT and mangrove are 44.02% and 46.70%, respectively.

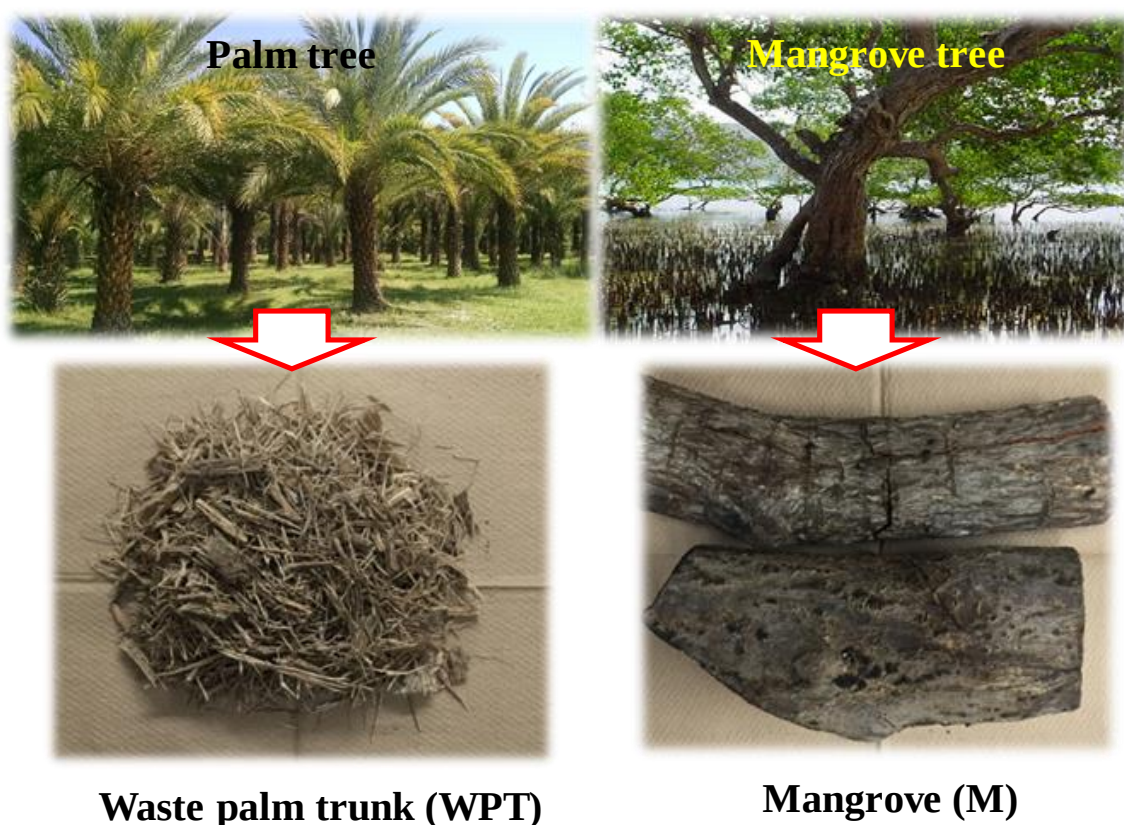


Fig. 3.1 Pictorial view of two raw biomasses employed for synthesis of functional ACs.

Table 3.1 Elemental compositions of waste palm trunk (WPT) and mangrove (M).

Raw material	Elemental composition [%]				Ash [%]
	C	H	N	O _{diff.}	
WPT	44.02	5.75	0.49	48.41	1.33
M	46.70	6.04	0.14	45.98	1.14

3.2.2 Experiments

3.2.2.1 Carbonization

The main purpose of carbonization is to remove the volatile matters from the biomass in order to convert it to a suitable form for activation. During the phase of the carbonization, the carbon content of the product attains a value of near about 80 percent. Most of the non-carbon elements, hydrogen, and oxygen are removed in gaseous form

during the carbonization process. Before carbonization, WPT and mangrove are crushed into a particle size less than 5 mm in order to perform homogeneous drying and carbonization. Then the crushing samples are dried in an air dryer at 100°C for 48 hours. Vacuum drying at 105°C for 1 hour is accomplished after air-drying before being used for carbonization. These two drying operations are assisted to remove water or moisture content from the two biomasses. The photographs of crushing and drying of two kinds of biomasses are shown in Fig. 3.2. The carbonization process for both biomasses is carried out at 500 and 600°C at a heating rate of 10°C/min with N₂ flow rate of 100 cc/min for 1 hour. The sample preparation scheme of ACs from biomass is shown in Fig. 3.3 [113]. The carbonization reactor chamber is shown in Fig. 3.4. It mainly consists of the high-temperature furnace with a temperature controller, stainless steel tube, and N₂ gas tank. The rotameter is used to control the N₂ flow rate inside the reactor chamber. Fig. 3.5 shows the photograph of two carbonized biomasses. After the heat treatment, biomass-derived carbonized samples are grinded and sieved to mesh size 100 µm for the application of the adsorption heat pumps. The resulting carbonized products have a small adsorption capacity, which is not suitable for AHP. To enhance the adsorption capacity, the further activation process is conducted, which in turn to increase the surface area and micropore volume of the activated carbons.

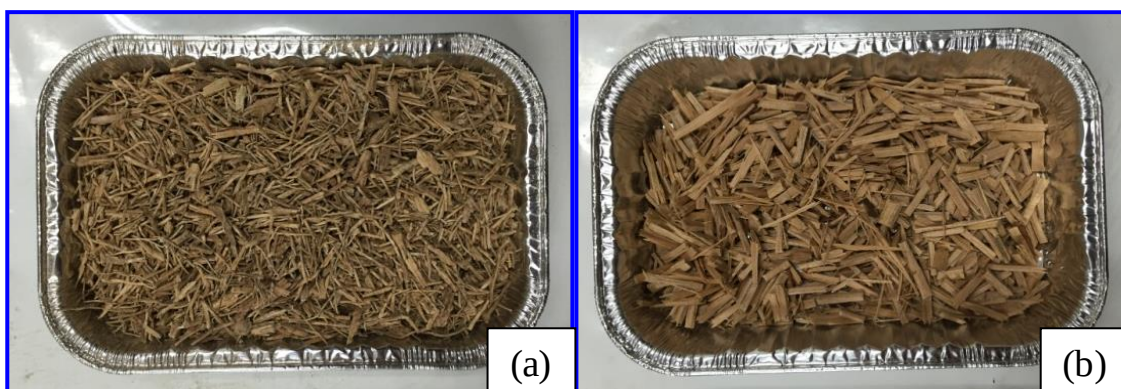


Fig. 3.2 Crushing and drying (a) WPT and (b) Mangrove.

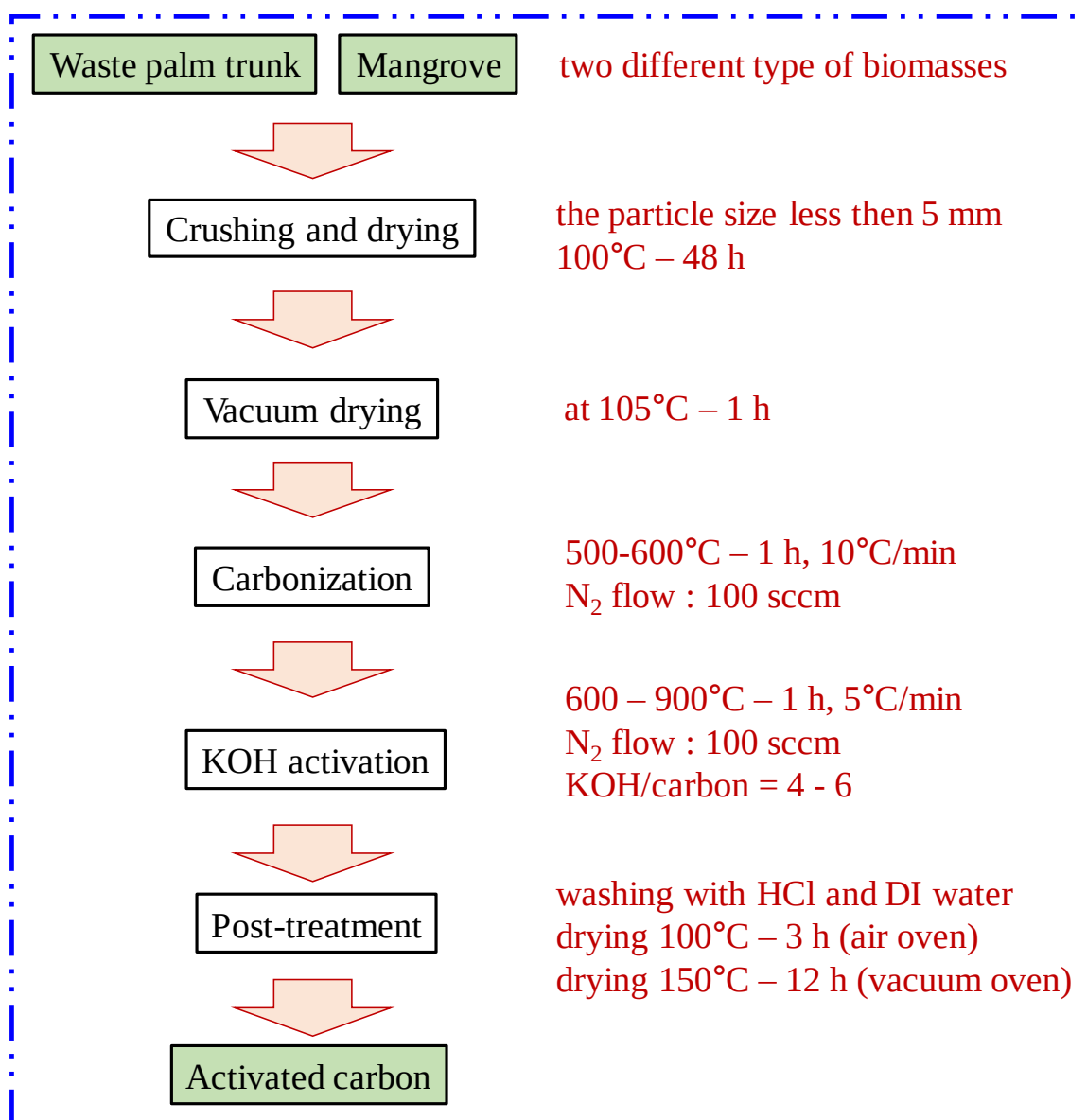


Fig. 3.3 Processing steps for preparation of biomass-derived activated carbons [113].

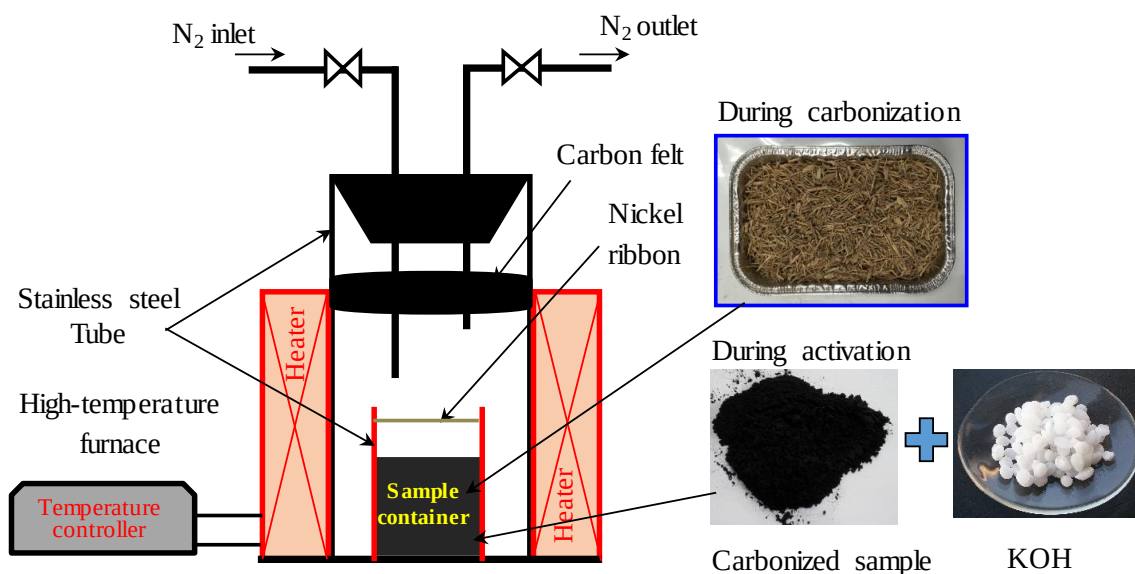


Fig. 3.4 Schematic diagram of experimental setup for carbonization and KOH activation reactor.



Fig. 3.5 Photograph of carbonized (a) WPT and (b) Mangrove

Carbonized products are produced from natural starting materials of WPT and mangrove. The elemental compositions (Carbon, Hydrogen, and Nitrogen) are analyzed using CHN analyzer (MT-5) supplied by Yanako, Japan. Typically, a carbonized product comprises high carbon content about 70-90%. Table 3.2 indicates the elemental composition of carbonized WPT and mangrove. The carbon content of these two samples

is increased after carbonization. The results show that the carbonized WPT comprises 72.35% C, 2.97% H, 0.48 % N, and 4.64% ash. It is noted that mangrove shows high carbon (81.91%) and low ash (3.64%) content compared to the WPT. From CHN analysis, it is concluded that high carbon and low ash content of both materials are suitable for making activated carbons.

Table 3.2. Elemental compositions of carbonized WPT and mangrove at 500°C.

Sample	Elemental composition [%]				Ash [%]
	C	H	N	O _{diff.}	
WC500	72.35	2.97	0.48	19.56	4.64
MC500	81.91	3.20	0.28	10.97	3.64

3.2.2.2 Activation

Carbonized WPT and mangrove are used for preparing activated carbons using chemical activation method. Particle size less than 100 μm of these two carbonized samples is used for activation. The activation process is carried out in nitrogen (N_2) atmosphere that acts as an inert medium. The identical activation conditions are applied to both carbonized materials (WPT and M). Fig. 3.3 describes the processing steps for preparation activated carbons from carbonized sample [113]. The chemical activation of various carbon sources using KOH as an activating agent is very promising because of its lower activation temperature and higher yields, and well-defined micropore size distribution and ultrahigh specific surface area up to 3000 $\text{m}^2 \text{g}^{-1}$ of the resulting activated carbons [31,116,124]. The same experimental setup (Fig. 3.4) is used for the preparation of ACs. KOH (purity > 85.0%, Wako Pure Chemical Industries, Ltd.) is selected as an activating agent in the impregnated WPT and mangrove biochar because it is found to be more effective than another chemical agent such as ZnCl_2 and H_3PO_4 for creating porosity in ACs. The experimental conditions such as temperature, activating agent (KOH), heating rate, holding time, N_2 flow rate are kept identical for preparation of activated carbons from both carbonized materials of WPT and M. The effects of various preparation conditions, including different activation temperatures (600-900°C), the impregnation ratios of KOH/WPT or M biochar (4:1 and 6:1) are studied in order to establish the optimum

conditions for producing high adsorption ability, large surface area with micropore, and micropore volume of ACs. The activation process can be explained as follows: firstly, the weight ratio of KOH/carbonized biomass is set to 4 or 6 and put into the stainless steel tube. KOH and carbonized biomass are then mixed inside the tube. After that, the stainless steel container is placed into an electric furnace vertically. The mixture is heat-treated up to 600°C at a heating rate of 5°C/min and maintained at 600°C for one hour under N₂ flow rate 100 cc/min. After the activation, the remaining KOH and salts formed during the heat treatment are removed by the washing with HCl solution for three times and deionized water once to adjust pH to be about 7. Finally, washing, the collected samples are dried at 100°C for 3 hours in an air oven and dried again at 150°C for 12 hours in a vacuum oven. A similar procedure is used for any other activation temperature. Total 12 samples, six from each type biomass (WPT and M) are prepared as can be seen in Table 3.3. Prepared activated carbons are then characterized using N₂ adsorption/desorption isotherms for calculating the porous properties and scanning electron microscope (SEM).

Table 3.3 Series of AC samples are prepared from WPT and M by changing carbonization and activation conditions.

No.	Carbonization temperature [°C]	Activation temperature [°C]	Heating rate [°C/min]	Holding time [h]	KOH: Sample	Sample naming
1		600			4:1	WC500A600K4
2		700			4:1	WC500A700K4
3	500	800	5	1	4:1	WC500A800K4
4		900			4:1	WC500A900K4
5		900			6:1	WC500A900K6
6	600	900			6:1	WC600A900K6
1		600			4:1	MC500A600K4
2		700			4:1	MC500A700K4
3	500	800	5	1	4:1	MC500A800K4
4		900			4:1	MC500A900K4
5		900			6:1	MC500A900K6
6	600	900			6:1	MC600A900K6

W: Waste Palm Trunk (WPT); M: Mangrove; C: Carbonization; A: Activation; K: KOH

3.2.3 Characteristics of synthesized AC samples

Nitrogen (N₂) adsorption/desorption onto twelve AC samples from both biomasses have been performed to investigate the influence of activation conditions on porous properties. To know the surface morphology of all AC samples SEM images are taken. Among these series of samples, two best AC samples are selected for knowing the particle size distribution. In addition, thermal conductivity is also investigated in all AC samples.

3.2.3.1 Porous properties

There is no simple quantitative theory for predicting adsorption isotherms in detail from known parameters. However, most of the gas and/or vapor adsorption isotherms can be categorized by means of IUPAC classification scheme, which has six types of isotherm for solid/gas. Isotherms of type I are generally true for microporous adsorbents for subcritical and supercritical conditions. Type I isotherm is suitable for AHP applications. Nitrogen adsorption is one of the standard procedures to determine the porous structure of carbonaceous adsorbents, which includes the surface area of pores, pore volume, and pore size. Nitrogen (N₂) adsorption isotherms are measured at 77 K using volumetric adsorption equipment (Belsorp-Max-S) supplied by BEL Japan Inc., Japan. The N₂ adsorption/desorption isotherms of WPT and M-derived ACs are shown in Fig. 3.6 and Fig. 3.7, respectively. A sharp increase in the N₂ adsorption amount at very low relative pressure ($P/P_0 \leq 0.01$) is a characteristic feature of microporous materials, which is observed for all AC sample for both types of biomasses. From the N₂ adsorption and desorption isotherms at 77 K, it is also confirmed that biomass-derived AC has not only micropores but also some fraction of mesopores. In addition, there is no significant hysteresis in the adsorption isotherms. As can be seen from these figures that N₂ adsorption quantity increases with increasing the activation temperature and KOH ratio. Total surface area, external surface area, total pore volume, micropore volume, and average pore width are evaluated using BET, NLDFT, and alpha-s method from N₂ adsorption isotherm at 77K.

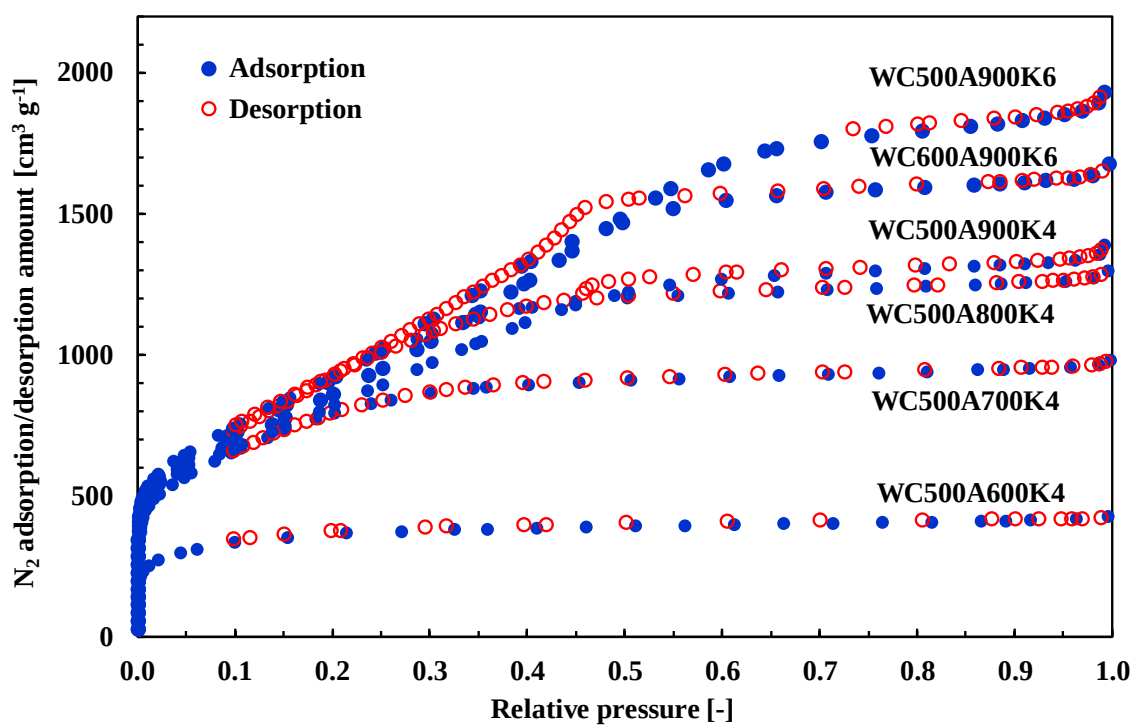


Fig. 3.6 N₂ adsorption/desorption isotherms of WPT-derived ACs at 77 K.

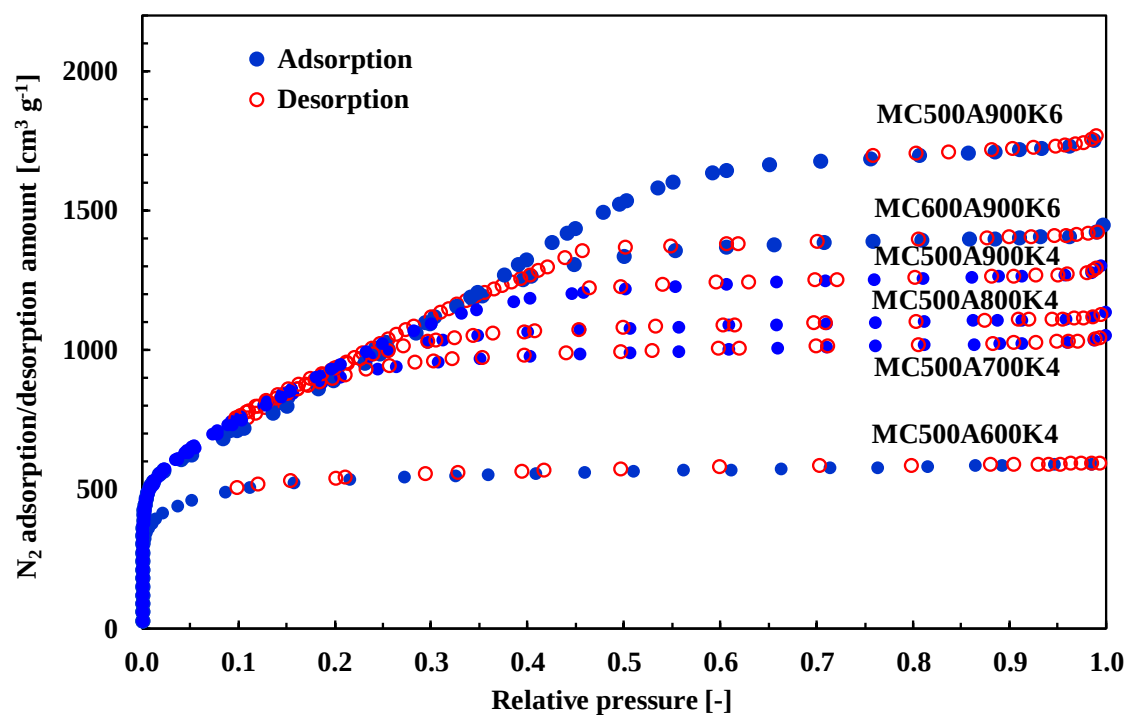


Fig. 3.7 N₂ adsorption/desorption isotherms of M-derived ACs at 77 K.

Fig. 3.8 and Fig. 3.9 show the pore size distribution of WPT and M-derived all AC samples respectively. Non-local density functional theory (NLDFT) has been used to estimate pore size distribution. It can be seen from these figures that pore size distribution changes with the changing of activation conditions, and their pore size is less than 5 nm.

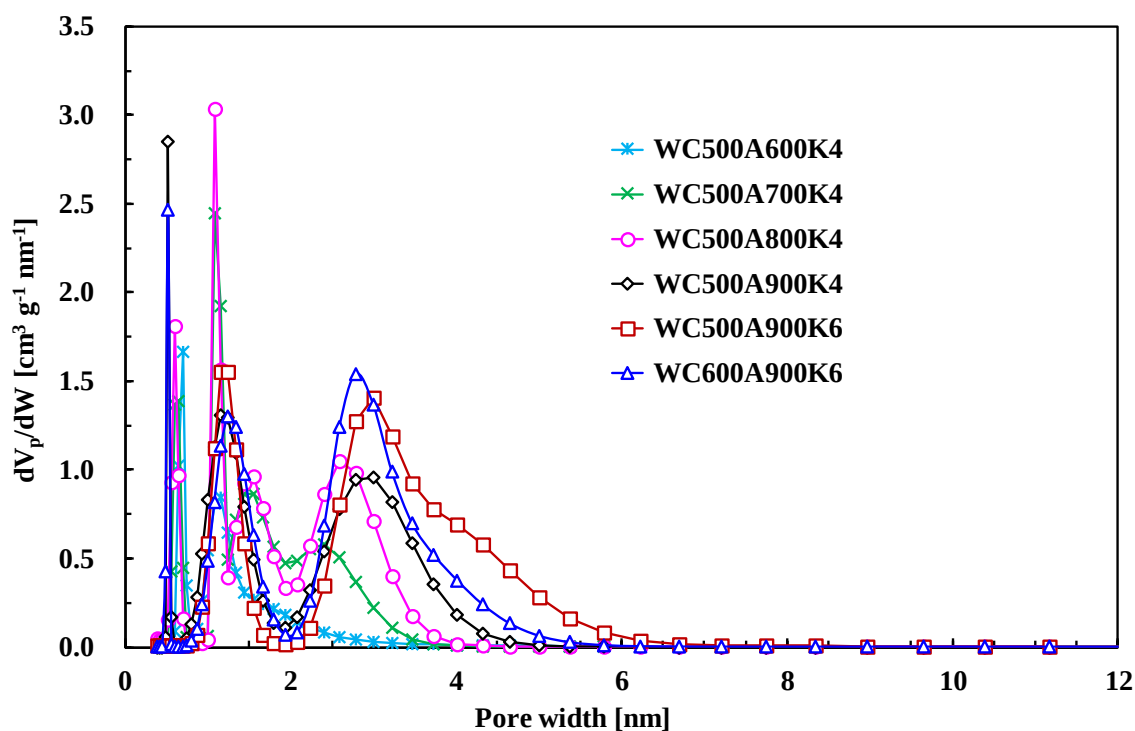


Fig. 3.8 Pore size distribution of WPT-derived ACs.

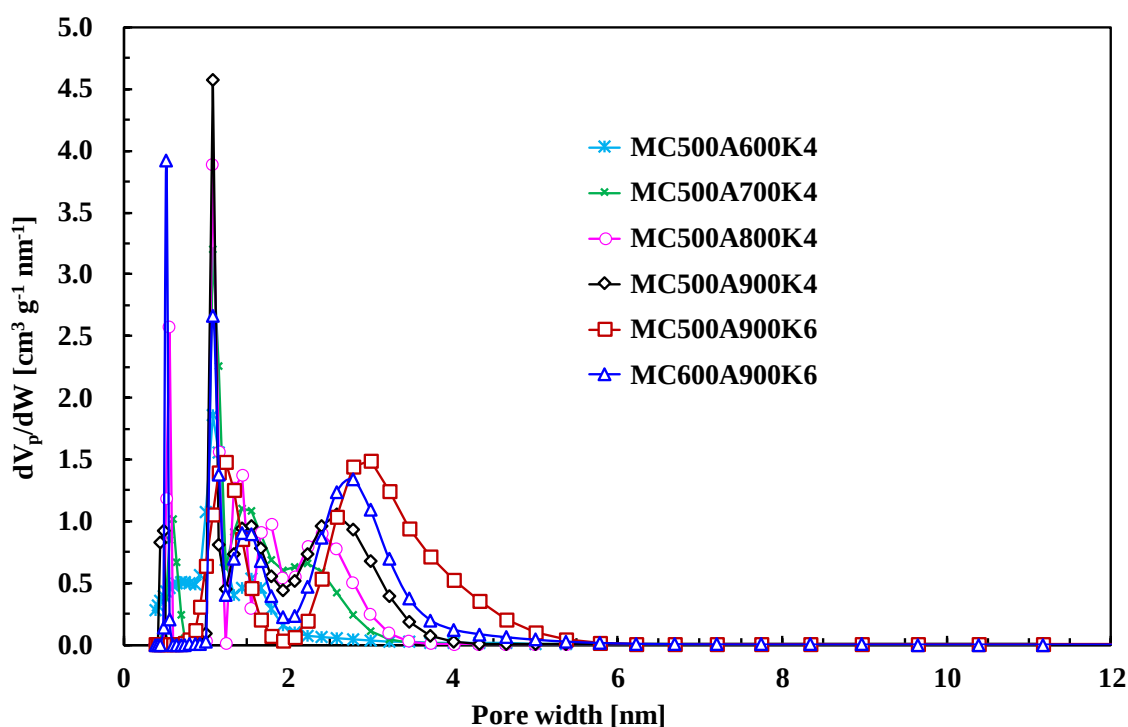


Fig. 3.9 Pore size distribution of M-derived ACs.

Finally, physical characterization results such as total BET surface area, external surface area, total and micropore volume, activation yield, and an average pore size of all AC samples derived from WPT and M are summarized in Table 3.4. From the experiment, it is found that carbonization at 500 and 600°C, activation at 900°C, and six times KOH create highest surface area and a pore volume from both kinds of biomasses. Figures 3.10–3.12 represents the influence of activation temperature, KOH ratio and carbonization temperature on total BET surface area, total pore volume and average pore size, respectively. The surface area of both kinds of ACs increases with the increasing of activation temperatures (Fig. 3.10). It is observed that at 600°C, surface area is about 2100 m² g⁻¹, however, after increasing the activation temperature, surface area increases to a significant value. In addition, it is noticed that surface area is almost saturated after activation temperature from 700°C even though at different carbonization temperature and KOH ratio in the case of M-derived ACs, which is more than 2900 m² g⁻¹ (Fig. 3.10). The similar phenomena are also observed in the case of WPT-derived ACs since activation temperature influence on the increase of surface area (Fig. 3.10). However, values quite fluctuate and at the beginning, the surface area is less compared to M-derived AC. It is also noticed that at high activation temperature and KOH ratio, surface area increased to

very large value and saturated which is the same as M-derived AC (Fig. 3.10). Pore volume and average pore width also increase with activation temperature and KOH ratio for both biomass-derived AC samples. However, it is observed that at a severer condition, which means at higher carbonization temperature (600°C), activation temperature (900°C) and 6 times KOH, the pore volume, as well as pore size, quite decreases.

Table 3.4 Pore structural parameters of WPT and mangrove-derived ACs that prepared at various activation conditions.

Sample	Total surface area [m ² g ⁻¹]	External surface area [m ² g ⁻¹]	Micropore volume [cm ³ g ⁻¹]	Total pore volume [cm ³ g ⁻¹]	Average pore width [nm]	Activation yield [%]
WC500A600K4	1402	14.10	0.62	0.65	0.90	50.17
WC500A700K4	2583	22.93	1.44	1.48	1.13	43.04
WC500A800K4	2985	32.28	1.90	1.96	1.29	37.87
WC500A900K4	2771	46.33	1.99	2.07	1.46	30.99
WC500A900K6	2848	103.99	2.69	2.87	1.96	20.54
WC600A900K6	2927	62.52	2.41	2.51	1.68	27.27
MC500A600K4	2131	10.68	0.90	0.91	0.84	54.61
MC500A700K4	2878	17.47	1.56	1.60	1.09	49.84
MC500A800K4	2919	20.09	1.69	1.72	1.16	52.46
MC500A900K4	2925	28.21	1.92	1.97	1.33	41.03
MC500A900K6	2911	58.99	2.58	2.68	1.81	32.14
MC600A900K6	2924	34.19	2.13	2.18	1.47	37.54

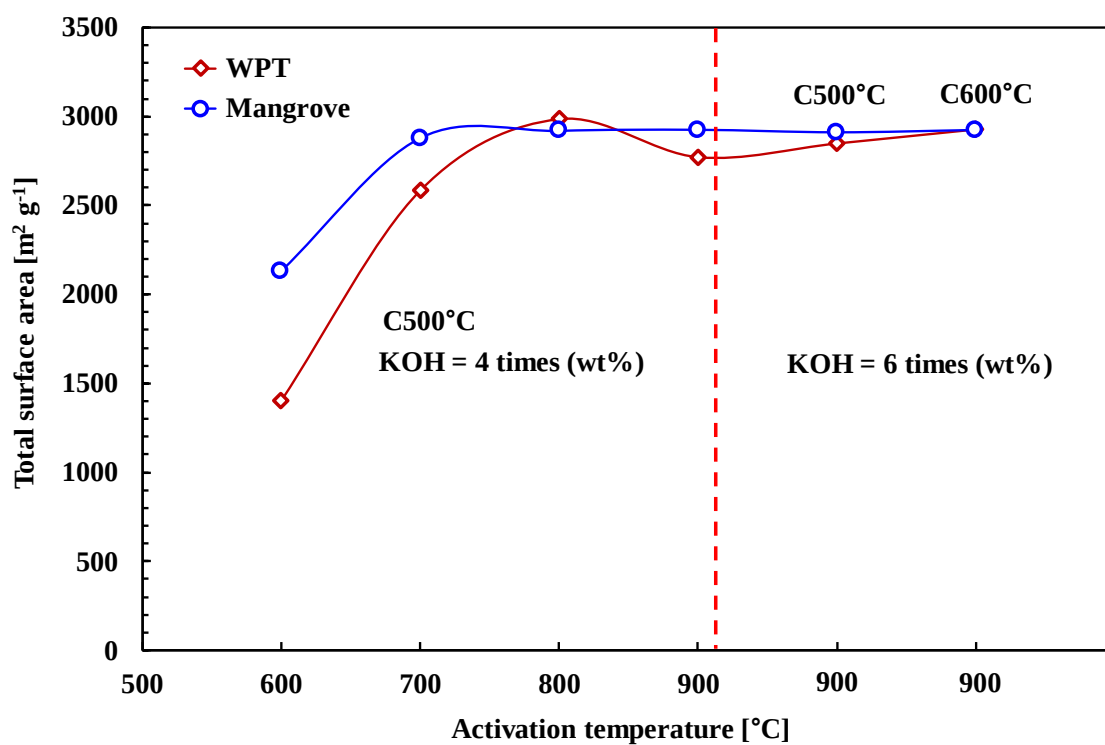


Fig. 3.10 Influence of activation temperature on surface area.

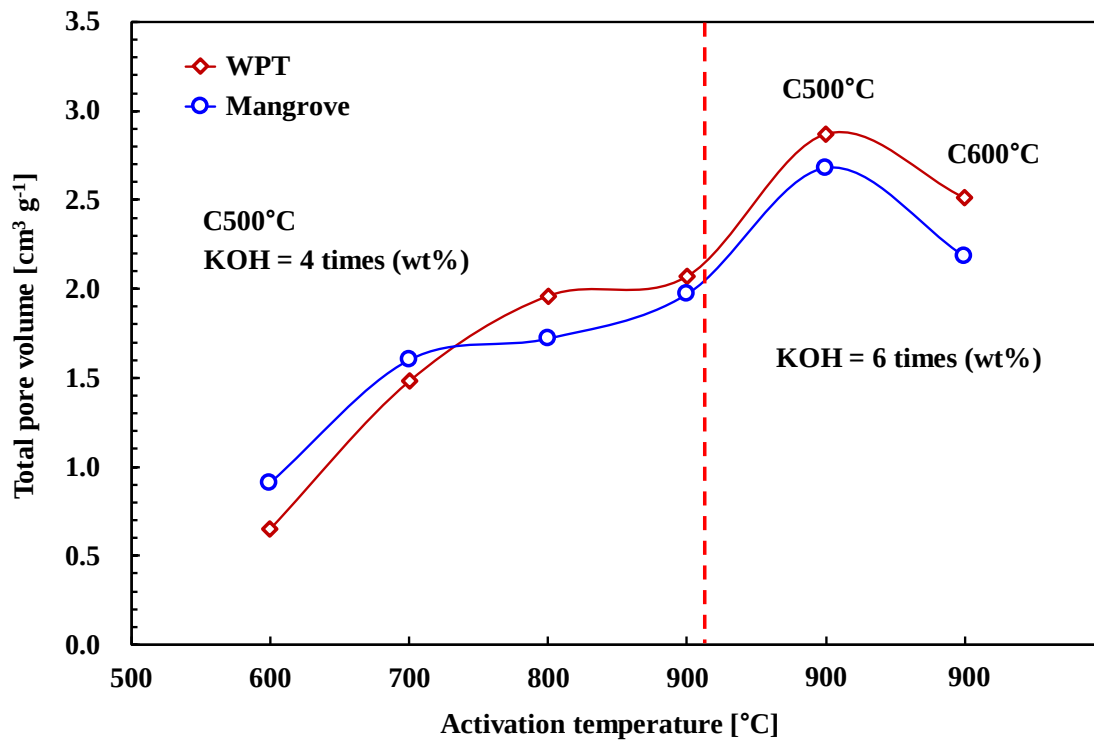


Fig. 3.11 Influence of activation temperature on pore volume.

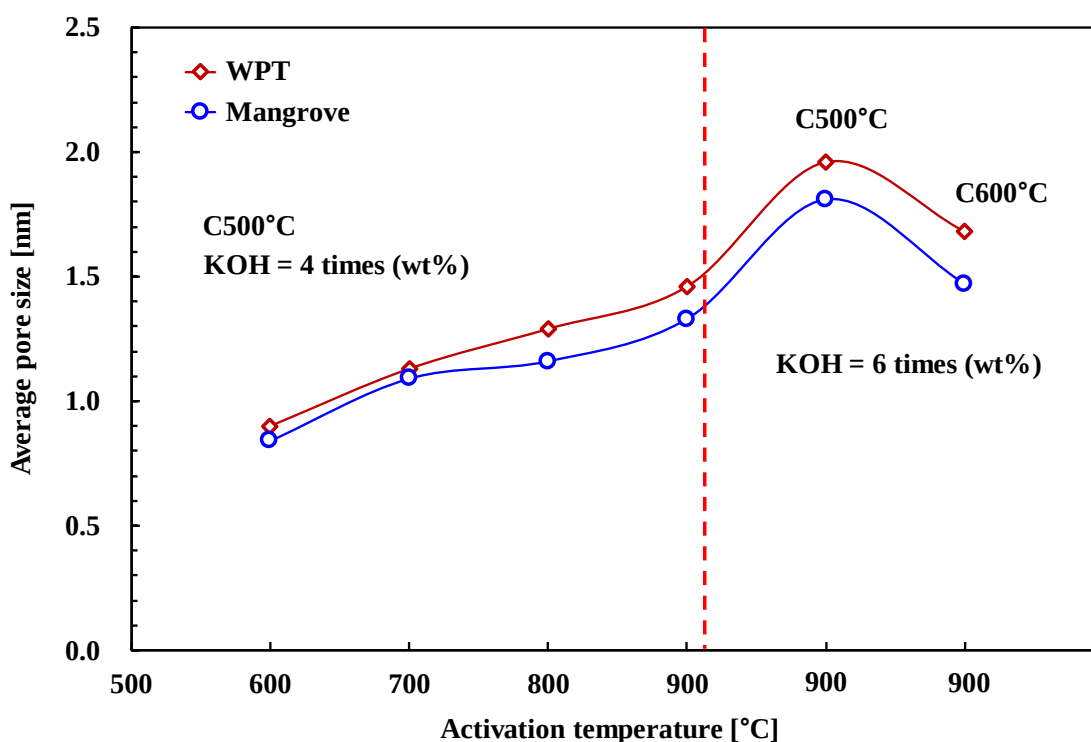


Fig. 3.12 Influence of activation temperature on average pore width.

3.2.3.2 Scanning electron microscopy (SEM) observation

The porous structure and chemical nature of synthesized ACs are a function of the precursor materials, the activation methods and the extent of activation. This is the reason why surface area or pore volume of ACs can vary widely from one kind to another. Pore structures of all prepared AC samples are investigated by scanning electron microscope (SEM), which are described in this section. SEM is used to study the changing in morphology in the materials during carbonization and activation process. The WPT and mangrove clearly show the canal structure, which is an excellent texture for AC production as the activating agent could easily diffuse into the carbon micropores, develop a large surface area, and pore volume. During the carbonization, most of the non-carbon elements are removed with the basic skeleton of the polymer remaining, which produced a biochar retaining the shape of the biomass precursor and formed the initial porosity of the biochar. Fig. 3.13 and Fig. 3.14 represent that the morphology of the WPT and mangrove-derived all AC samples at various activation conditions. The synthesized ACs keeps their micro-structural feature even at severe conditions as can be seen from these figures.

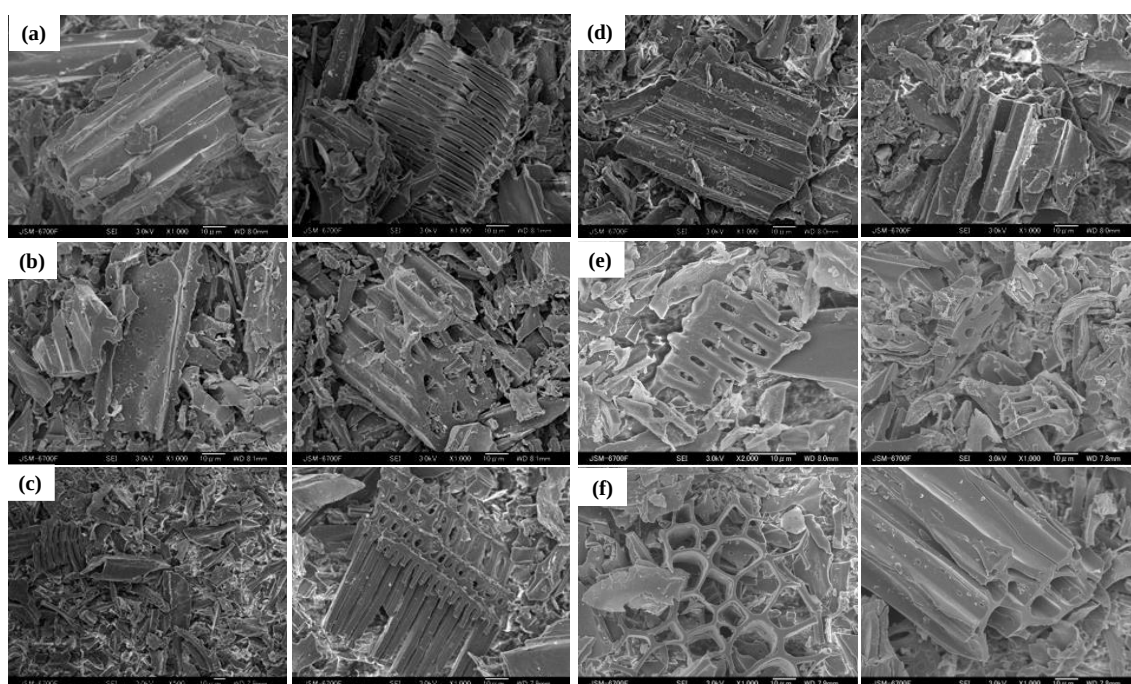


Fig. 3.13 SEM images of WPT-derived ACs (a) WC500A600K4; (b) WC500A700K4; (c) WC500A800K4; (d) WC500A700K6; (e) WC500A900K6, and (f) WC600A700K6

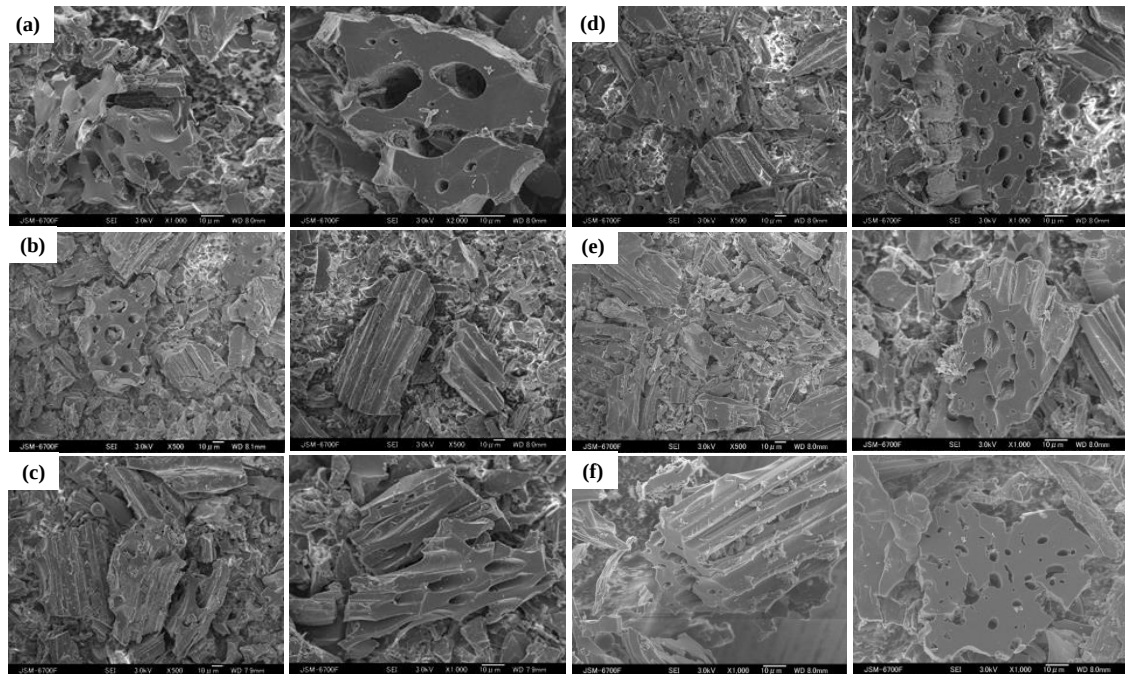


Fig. 3.14 SEM images of mangrove-derived ACs (a) MC500A600K4; (b) MC500A700K4; (c) MC500A800K4; (d) MC500A700K6; (e) MC500A900K6, and (f) MC600A700K6.

3.2.3.3 Thermal conductivity of biomass-derived ACs

The C-Therm TCi thermal conductivity analyzer has been employed in this study to measure the thermal conductivity of all WPT and M-derived AC powder samples. Thermal conductivity is measured at ambient condition. Fig. 3.15 and Fig. 3.16 show the thermal conductivity results of WPT and mangrove-derived ACs, respectively. As can be seen from these figures, thermal conductivity decreases with the increasing of porous properties for both kinds of AC samples. Thermal conductivity values vary from 0.054 to 0.041 $\text{W m}^{-1} \text{K}^{-1}$ for WPT-derived ACs whilst 0.061 to 0.045 $\text{W m}^{-1} \text{K}^{-1}$ is for M-derived ACs.

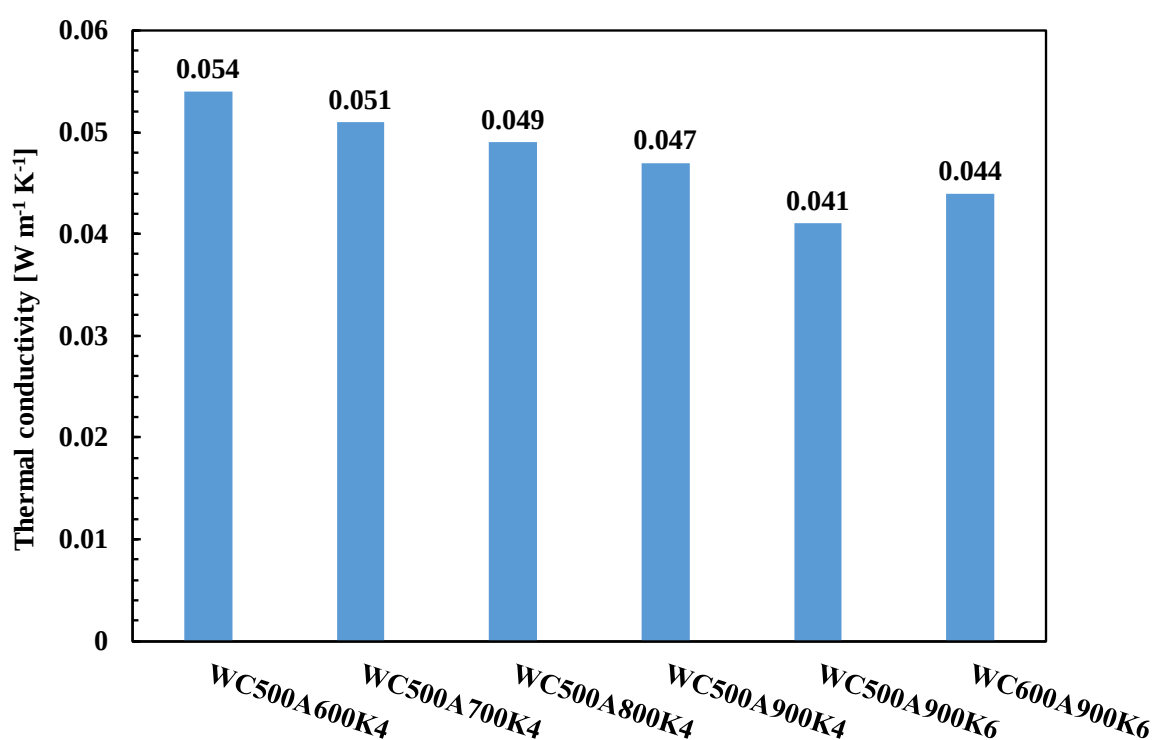


Fig. 3.15 Thermal conductivity of all WPT-derived ACs.

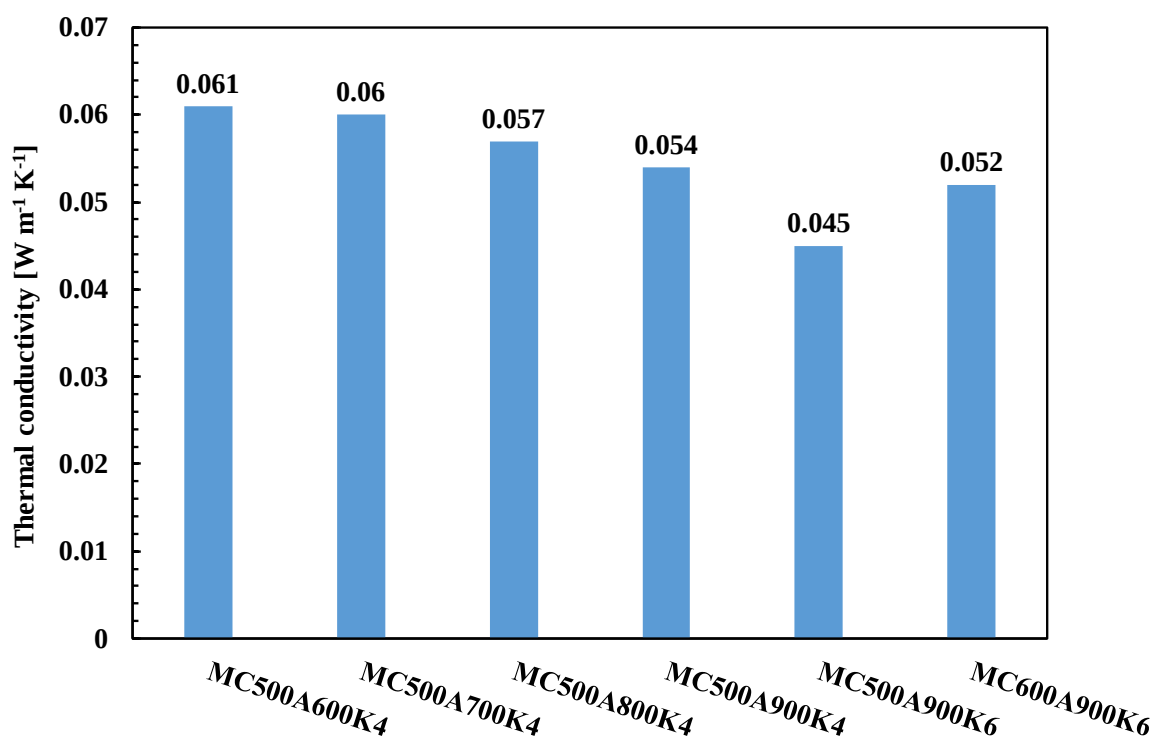


Fig. 3.16 Thermal conductivity of all M-derived ACs.

3.2.3.4 Choice of optimal AC

It is found that all porous properties are saturated at a particular condition and decreases at sever condition as discussed in section 3.2.3.1. Moreover, at the same time activation yield also decreases at higher temperature and KOH ratio, as can be seen from Table 3.4. It can be concluded that carbonization at 500 and 600°C, activation at 900°C, and six times KOH create highest surface area and a pore volume from both kinds of biomasses-derived ACs. Therefore, WC500A900K6, WC600A900K6, MC500A900K6, and MC600A900K6 are selected as a promising adsorbent for AHP application. Consequently, the subsequent chapter presents the further analysis such as adsorption (ethanol and CO₂) characteristics and thermodynamic analysis of these ACs for AHP application.

3.3 Synthesis and characterization of AC based composite adsorbents

Most of the parent adsorbents are either powder or granular forms such as activated carbon, silica gel, and zeolite. As a result, they possess very low thermal conductivity and volumetric cooling capacity because of their shape and low packing density. Therefore, cooling systems are bulky with a high cost, which hinders for spreading technology. Although activated carbon (AC) is a promising adsorbent for potential AHP systems because of high specific surface area and high adsorption uptake of refrigerant vapor [15,16,37,125]. Therefore, it is also very urgent necessary to enhance the thermal conductivity of AC powder and volumetric uptake for making system more compact and efficient. Recently, several researchers have reported that consolidated composite adsorbents can enhance the heat transfer inside the adsorber unit [70,89–91,118,121]. The consolidated composite adsorbent is a combination of a highly porous activated carbon powder (Maxsorb III), expanded graphite (EG)/graphene nanoplatelets (GNPs) as thermal conductivity enhancer and polyvinyl alcohol (PVA) as a binder. This section presents the preparation and characterization of composites through N₂ adsorption, porous properties, and thermal conductivity investigation.

3.3.1 Materials

3.3.1.1 Activated carbon (Maxsorb III)

The key material used for preparing consolidated composite adsorbents is AC powder, namely Maxsorb III provided by Kansai Coke & Chemicals Co. Ltd., Japan. Elemental composition of Maxsorb III is summarized in Table 3.5 [16]. The field emission scanning electron micrograph (FE-SEM) of the Maxsorb III is shown in Fig. 3.17 [15].

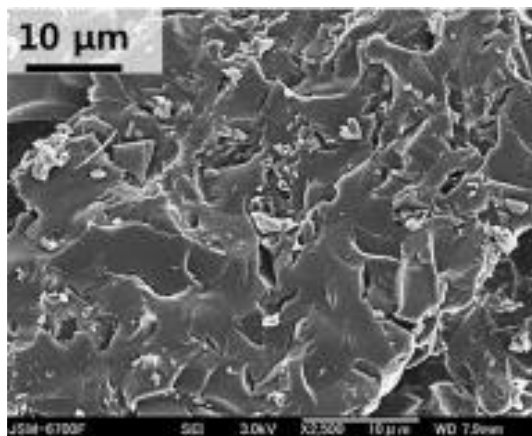


Fig. 3.17 SEM photograph of activated carbon powder (Maxsorb III) [15].

Table 3.5 Composition and porous properties of AC powder (Maxsorb III) [31,44,126].

Carbon [wt%]	95.13
Hydrogen [wt%]	0.14
Nitrogen [wt%]	0.25
O (diff.) [wt%]	4.35
Average particle diameter (μm)	100 (D_{50})
Specific heat capacity [$\text{J g}^{-1} \text{K}^{-1}$]	0.844 (30°C)
Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	0.066 (30°C)
Total BET surface area [$\text{m}^2 \text{g}^{-1}$]	3292 ± 39
Total pore volume [$\text{cm}^3 \text{g}^{-1}$]	1.71
Average pore width [nm]	1.12

3.3.1.2 Expanded graphite (EG)

Expanded graphite (EG) is employed as an additive into AC powder for enhancing the thermal conductivity. EG type EC500 is used as a thermal conductivity enhancer which is procured from Ito Graphite Industries Co., Ltd., Japan. Table 3.6 presents the thermo-physical properties of EC500 mentioned by the manufacturer. SEM photograph of EG is also presented in Fig. 3.18.

Table 3.6 Thermo-physical properties of EC500.

Carbon [wt%]	97.5
Ash [wt%]	0.14
Volatile content [wt%]	0.25
Average particle diameter [μm]	25
Specific heat capacity [$\text{J K}^{-1} \text{g}^{-1}$]	0.738
Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	0.105
Total BET surface area [$\text{m}^2 \text{g}^{-1}$]	99 ± 6
Total pore volume [$\text{cm}^3 \text{g}^{-1}$]	0.002

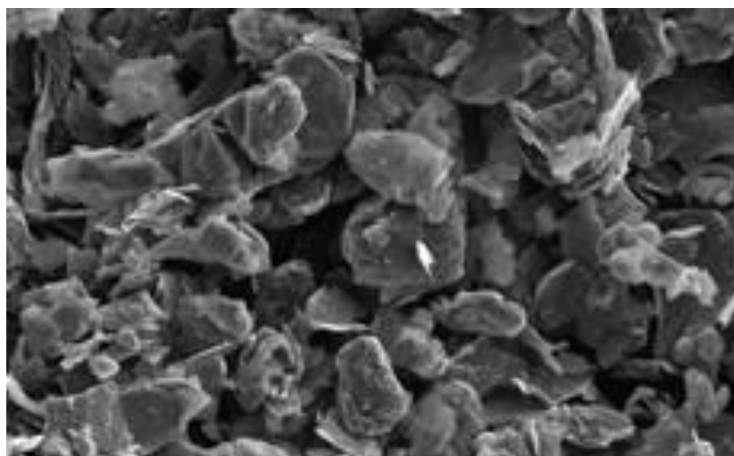


Fig. 3.18 SEM photograph of EG (EC500).

3.3.1.3 Graphene nanoplatelets (GNPs)

Two types of GNPs; H-grade (H25) and C-grade (C750) are obtained from XG Sciences for enhancing the thermal conductivity of composites [127]. The properties provided by the XG Sciences for each type of GNPs are shown in Table 3.7. The SEM images of GNPs (H25 and C750) are shown in Fig. 3.19.

Table 3.7 Technical specifications of graphene H-grade (H25) and C-grade (C750) [127].

Property	H25	C750
Particle thickness [μm]	25	few nanometers
Particle diameter [nm]	15	< 2
Shape	platelet	platelet
Appearance	black granules	black granules/powder
Bulk density [g cc^{-1}]	0.03 to 0.1	0.2 to 0.4
Total BET surface area [$\text{m}^2 \text{g}^{-1}$]	44 ± 0.45	777 ± 6
Total pore volume [$\text{cm}^3 \text{g}^{-1}$]	0.065	1.097

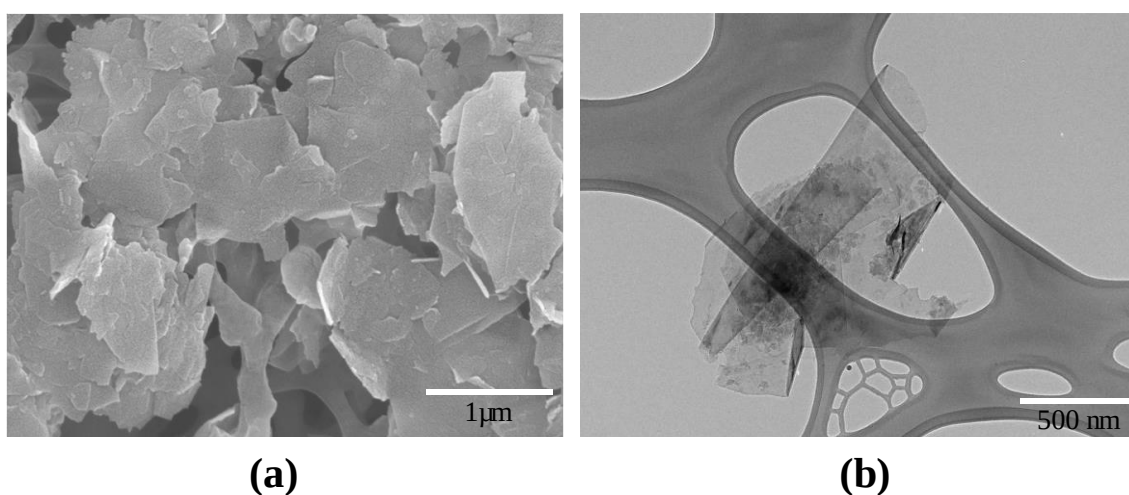


Fig. 3.19 SEM photograph of GNPs; (a) H25 and (b) C750 [127].

3.3.1.4 Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) 500 supplied by Kanto Chemical Co., Inc., Japan is used as a binder. It is a granular type, white-pale yellow color, odorless material [128]. Table 3.8 represents the thermo-physical properties of PVA provided by the supplier.

Table 3.8 Thermo-physical properties of PVA.

Chemical formula	$(-\text{CH}_2\text{CH}(\text{OH})-)_{\text{n}}$ ($\text{n} = 500$)
Specific heat capacity [$\text{J g}^{-1} \text{K}^{-1}$]	0.816 at 30°C
Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	0.31 ± 0.002 [129]
Total BET surface area [$\text{m}^2 \text{g}^{-1}$]	126 ± 3
Total pore volume [$\text{cm}^3 \text{g}^{-1}$]	0.104
Melting point [$^\circ\text{C}$]	300
Solubility in solvents	water
Degree of hydrolysis [%]	86.5-89.0



Fig. 3.20 Photograph of Polyvinyl alcohol (PVA).

3.3.2 Composite adsorbents using EG as a thermal conductivity enhancer

Fig. 3.21(a) shows the preparation process of the composite adsorbents. The process can be explained as follows; firstly, AC type Maxsorb III and expanded graphite (EG) type EC500 are dried in the oven at a temperature of 120°C for about 6 hours to eliminate the moisture content. The binder of type PVA that exists in a powder form is mixed with water where it turns into a solution. Maxsorb III and EG powders, with certain ratios, is then mixed with the binder solution. It should be highlighted that mass of water is almost two times of the total mass of composite including Maxsorb III, EG, and binder. After that, the mixture is compressed using a pressing machine. Finally, the composite adsorbent samples are dried in the oven at a temperature of 120°C for about 10 hours. Two types of composite samples have been prepared based on the sample mass and size. The first type is used for ethanol adsorption uptake measurements where the dry samples mass is about 2 g, and diameter is 20 mm whilst the sample height ranging from 12 mm to 15 mm based on the composition of the composite. The second type is used for nitrogen (N₂) adsorption and thermal conductivity measurements. A series of composite samples have been prepared where the samples dry mass is about 0.2 g; the diameter is 17 mm and height ranging from 1.1 to 1.6 mm. A pictorial view of developed composite adsorbents is shown in Fig. 3.21(b). The list of all prepared composites is summarized in Table 3.9 including the composition ratios of all mixing materials.

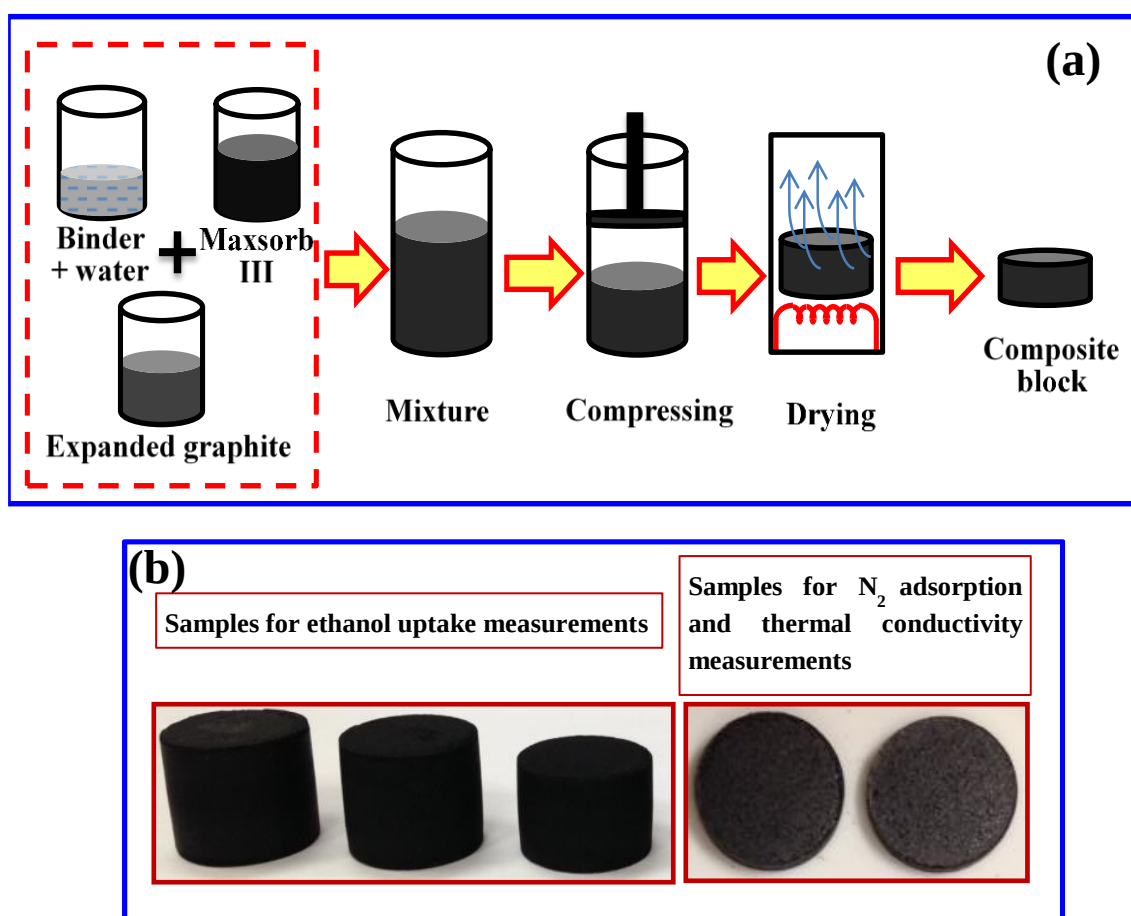


Fig. 3.21 (a) Production process of synthesized composite adsorbents, (b) a pictorial view of synthesized composite adsorbents.

Table 3.9 List of prepared consolidated composites.

Name	Maxsorb III	PVA	EC500
A	50 wt%	10 wt%	40 wt%
B	60 wt%	10 wt%	30 wt%
C	70 wt%	10 wt%	20 wt%
D	80 wt%	10 wt%	10 wt%

3.3.3 Composite adsorbents using GNPs as a thermal conductivity enhancer

The same procedure and same experimental conditions as discussed in the previous section are applied for the synthesis of GNPs contained composites. A series of composites by changing the composition ratios of Maxsorb III and GNPs whilst PVA amount kept constant are prepared in which the composite dry mass is about 195 mg, the diameter is 17 mm and height ranging from 1.4 to 2.2 mm. Fig. 3.22 shows the synthesis procedure and the pictorial view of the some selected composites. The same composite is used for further characterization such as N₂ adsorption, ethanol and CO₂ adsorption, and thermal conductivity measurement. Table 3.10 presents the list of prepared composites with the composition ratios of mixing materials at same applied pressure.

Table 3.10 List of prepared consolidated composites.

Name	Maxsorb III	PVA	H25	C750
composite 1	90 wt%	10 wt%	-	-
composite 2	70 wt%	10 wt%	20 wt%	-
composite 3	50 wt%	110 wt%	40 wt%	-
composite 4	70 wt%	10 wt%	-	20 wt%

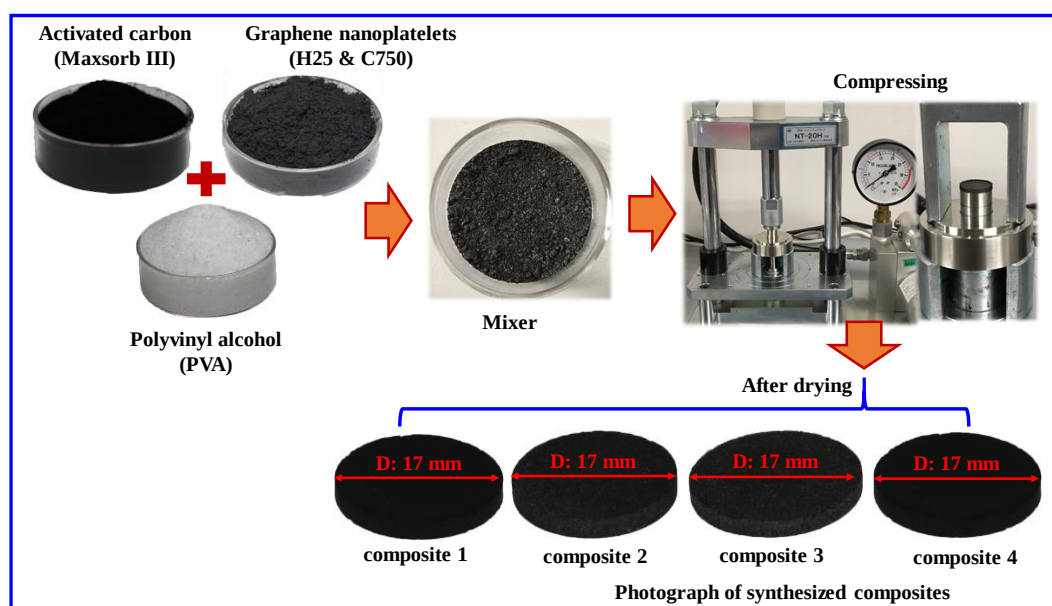


Fig. 3.22 Synthesis procedure and pictorial view of synthesized GNPs contained composites.

3.3.4 Experiments

3.3.4.1 N_2 adsorption

Nitrogen (N_2) adsorption onto the adsorbent is one of the standard methods to investigate the porous properties such as surface area, pore volume and pore size distribution of adsorbent material. The N_2 adsorption/desorption isotherm of synthesized composites has been investigated using volumetric method employing 3Flex™ Surface Characterization Analyzer as shown in Fig. 3.23. N_2 adsorption/desorption experiment is conducted at -196°C (77 K) after regeneration temperature of 250°C for 2 h. Brunauer-Emmett-Teller (BET) method has been used to calculate the surface area whereas the Non-Local Density Functional Theory (NLDFT) has been employed to estimate the pore size distribution and pore volume.

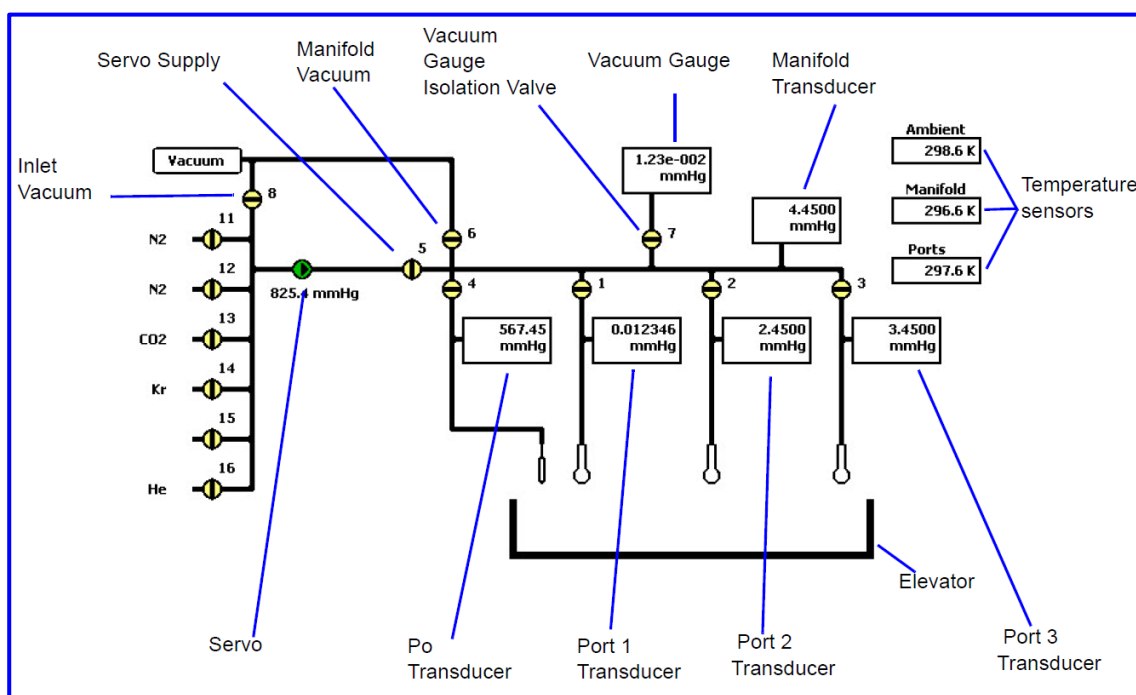


Fig. 3.23 Schematic diagram of 3Flex™ Surface Characterization Analyzer.

3.3.4.2 Thermal diffusivity and conductivity measurement of composites

The NETZSCH LFA 457 MicroFlash is employed to measure the thermal diffusivity and thermal conductivity of all synthesized composites. The simplified schematic diagram of LFA 457 is shown in Fig. 3.24. It consists of mainly laser source, furnace, IR detector, and data acquisition system [130]. The software package includes non-linear regression analysis to consider for radial and facial heat losses, finite-pulse effects, and internal radiative heat transfer. Measurements are carried out at room temperature to 100°C and atmospheric pressure. The measurement is conducted many times for each sample to check the repeatability.

The laser flash method is based on a transient heat flux technique for thermal diffusivity measurement. Parker et al. [131] first introduced this method in 1960. In this measurement, a short duration of high-intensity laser pulse hits the front side of the tested sample. The adsorbed heat travels through the sample thickness causing an increase the rear side temperature, which is detected by a detector with time. The temperature distribution in a thermally insulated sample is described by Carslaw and Jaeger [132]. Assuming that the initial temperature of the sample is T_0 the transient temperature distribution $T(x,t)$ across the sample thickness, L , after the applying of heat energy Q , can be obtained by solving the 1-D heat conduction equation.

$$\frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \quad \text{for } 0 < x < L \quad (3.1)$$

With the following initial and boundary conditions:

$$T(x, 0) = \frac{Q}{\rho C_p d} \quad \text{for } 0 < x < d \quad (3.2)$$

$$T(x, 0) = 0 \quad \text{for } d < x < L \quad (3.3)$$

$$\frac{\partial T(0, t)}{\partial x} = \frac{\partial T(L, t)}{\partial x} = 0 \quad \text{for } t > 0 \quad (3.4)$$

After solving the equation (3.1) using the equation (3.2) to (3.3), the temperature distribution at the rear side of the sample at time t is described by the following equation.

$$T(x, t) = \frac{Q}{\rho C_p L} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \pi^2 \alpha t}{L^2}\right) \right] \quad (3.5)$$

Where $T(x,t)$ is the temperature distribution across the sample thickness, L , after the applying of heat energy Q .

From the equation (3.5), 2-D parameters, Θ , and τ , may be defined as:

$$\Theta(L, t) = \frac{T(L, t)}{T_M} \quad (3.6)$$

$$\tau = \frac{\pi^2 \alpha t}{L^2} \quad (3.7)$$

Where, T_M is a maximum temperature at the rear face, and the equation (3.5) becomes:

$$\Theta(L, t) = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \tau) \quad (3.8)$$

At $t = 0.5$, the time required for the rear side temperature to reach half of the maximum temperature rise, $\tau = 1.38$, rearranging equation (3.7) thus yields:

$$\alpha = \frac{1.38 L^2}{\pi^2 t_{0.5}} = 0.1388 \frac{L^2}{t_{0.5}} \quad (3.9)$$

Thermal diffusivity is then determined by an equation (3.9) using the sample thickness and the value of $t_{0.5}$.

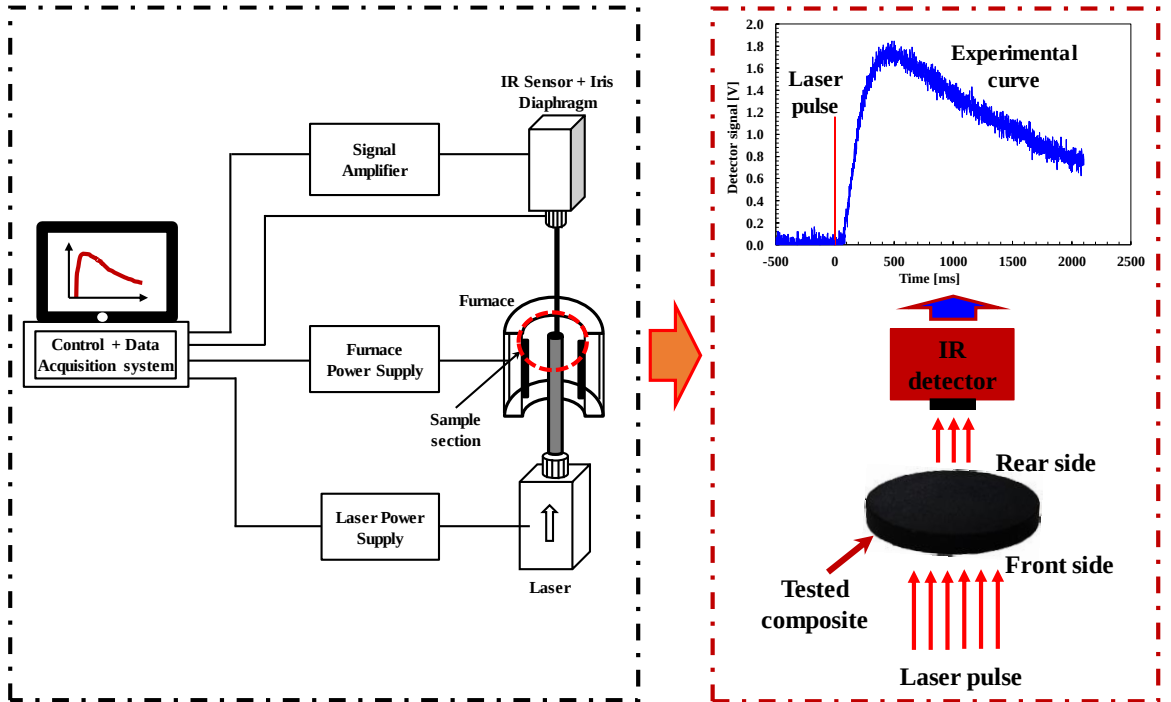


Fig. 3.24 Schematic design of LFA 457 MicroFlash system.

Fig. 3.25 represents the illustration of detector output from LFA 457 system for GNPs contained composite 2, composite 4. In LFA analysis software, Cowan + pulse correction model is used to fit the experimental data. It is seen that experimental data is well fitted with the model (Fig. 3.25) and $t_{0.5}$ can be calculated from the detector signal. Finally, the equation (3.9) gives the thermal diffusivity of the studied composite. It is observed that H-grade GNPs contained composite gives lower $t_{0.5}$, which implies higher diffusivity compare to C-grade (C750) contained composite.

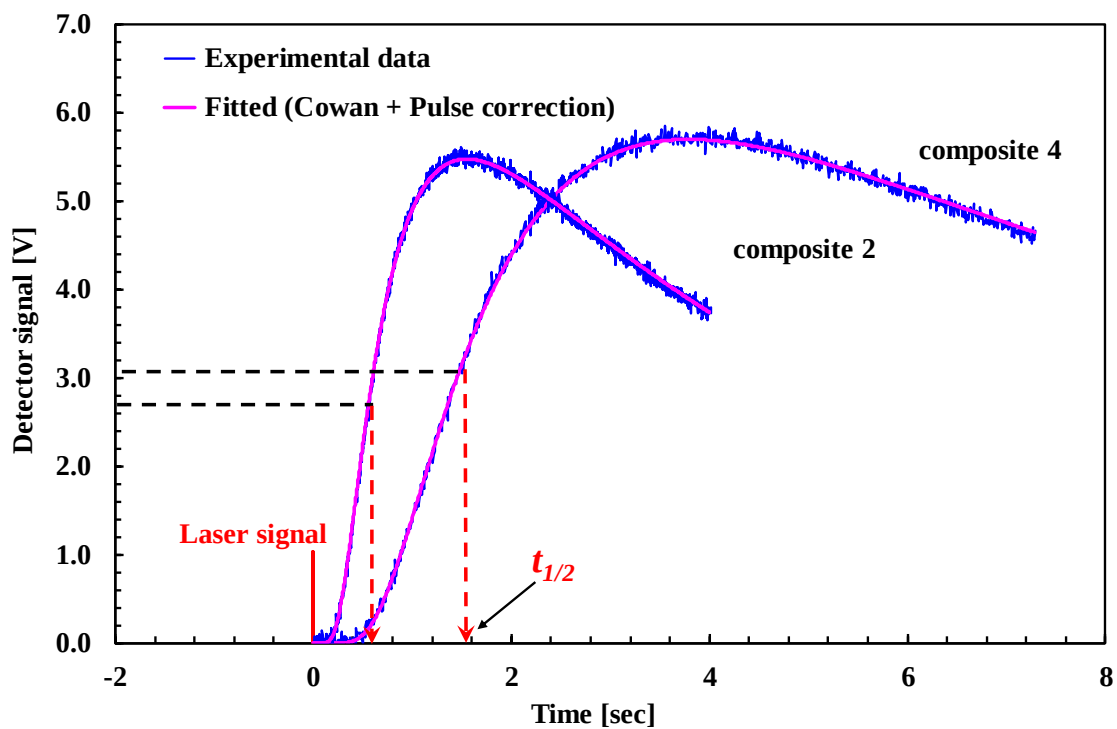


Fig. 3.25 An illustration of detector signal with a fitted model for GNPs contained composite 2 and composite 4.

The thermal conductivity of the composite adsorbent can be estimated using the equation (3.10) below.

$$k = \alpha \rho C_p \quad (3.10)$$

Where k denotes the thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$], α represents the thermal diffusivity of composite adsorbents [$\text{mm}^2 \text{s}^{-1}$], ρ is the adsorbent density [kg m^{-3}] and C_p stands for specific heat [$\text{J g}^{-1} \text{K}^{-1}$]. The specific heat of composites can be calculated according to the equation (3.11) below [46];

$$C_p = \left(\frac{1}{m_{\text{composite}}} \right) \sum m_i C_{p,i} \quad (3.11)$$

Where i presents the constituent of composites including Maxsorb III, EG/GNPs, and binder, whilst m stands for the mass of constitute.

3.3.5 Characteristics of synthesized composites

3.3.5.1 EG contained composites

3.3.5.1.1 Porous properties

The porous properties including total surface area, total pore volume, and pore size distribution of the prepared composite adsorbents named A, B, C, and D have been estimated from nitrogen adsorption isotherm. The compositions of the developed samples have been furnished in Table 3.11. Fig. 3.26 shows the N₂ adsorption/desorption isotherm of the studied composite adsorbents. It can be seen from Fig. 3.26 that the amount of N₂ adsorbed increases with the increase of the percentage of Maxsorb III, and no hysteresis has been observed. The surface area of each composite adsorbent has been investigated using Brunauer-Emmett-Teller (BET) method whilst the Non-Local Density Functional Theory (NLDF) has been used to estimate the total pore volume. The pore size distribution analysis using the NLDF theory for composite adsorbents A, B, C, and D are presented in Fig. 3.27 and results showed that their range of pore diameters is between 10 Å and 35 Å. Numerical values of the total surface area and total pore volume of the tested composites have been presented in Table 3.11. It should be highlighted that the porous properties of the tested composites in terms of surface area and pore volume depends mainly on the percentage of the Maxsorb III.

Table 3.11 Composition and porous properties of the developed consolidated adsorbent samples.

Sample composition	Total surface area [m ² g ⁻¹]	Total pore volume [cm ³ g ⁻¹]
A: 50% Maxsorb III, 40% EG, 10% binder	1420 ± 30	0.787
B: 60% Maxsorb III, 30% EG, 10% binder	1907 ± 21	0.948
C: 70% Maxsorb III, 20% EG, 10% binder	2000 ± 34	1.094
D: 80% Maxsorb III, 10% EG, 10% binder	2485 ± 19	1.210

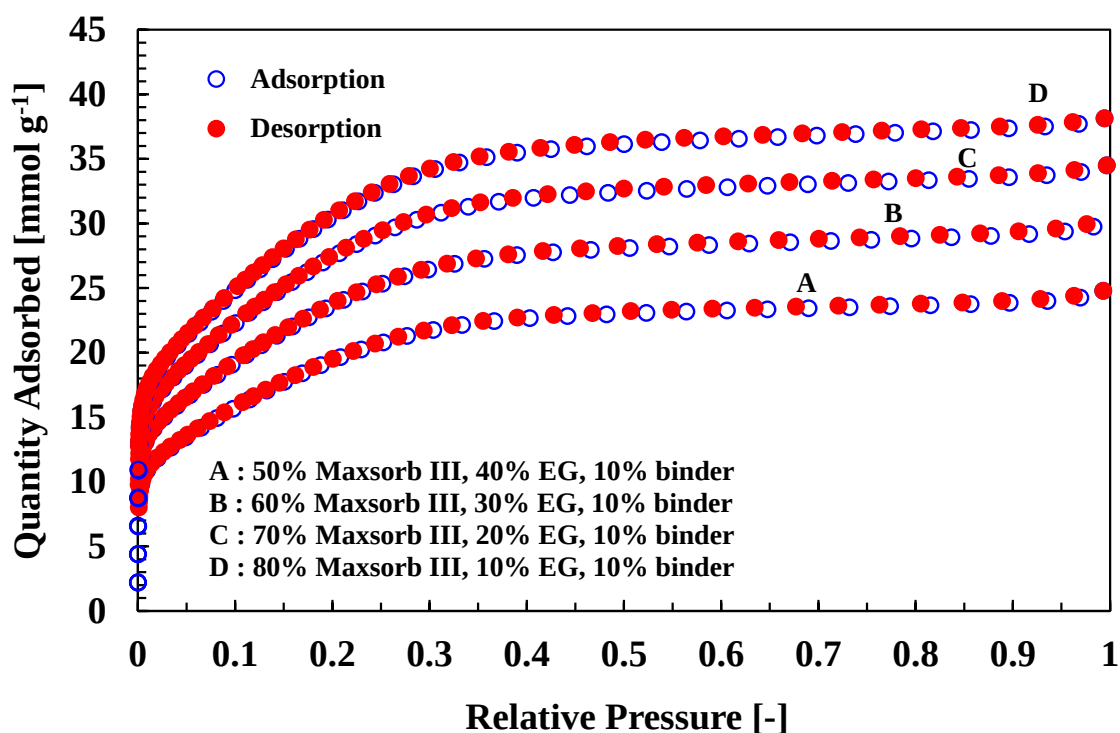


Fig. 3.26 Nitrogen adsorption/desorption isotherm onto various composites.

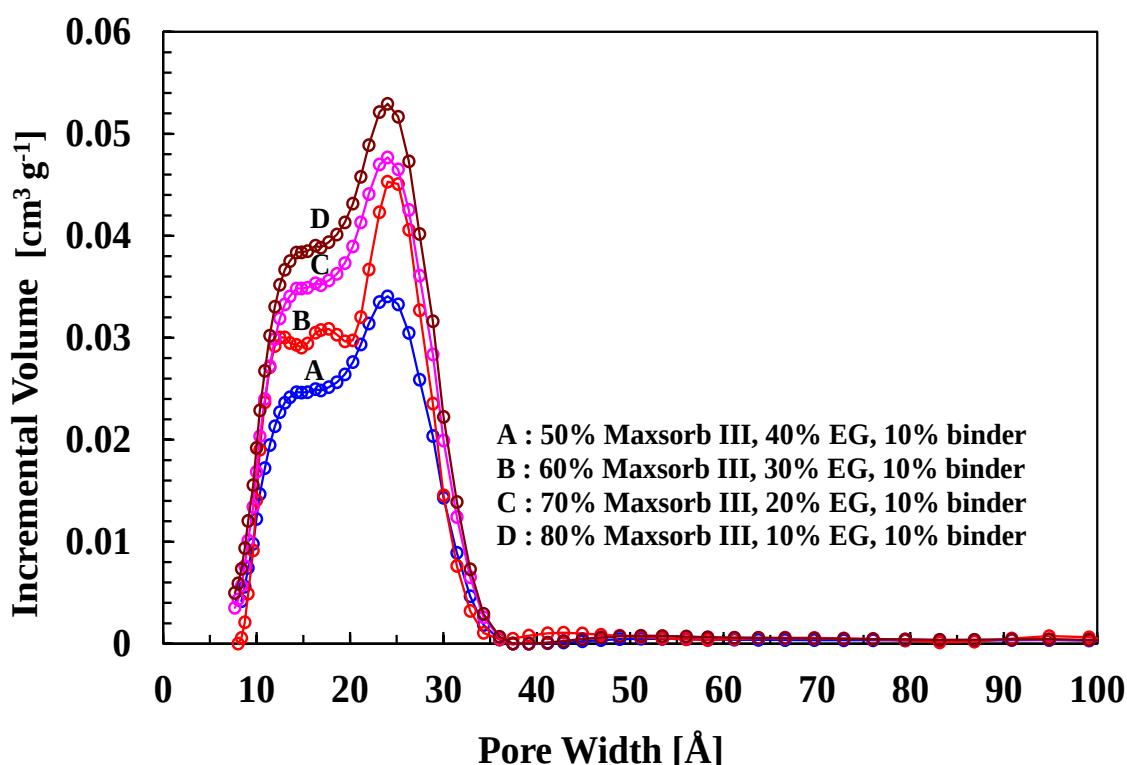


Fig. 3.27 The pore size distribution of various consolidated composite samples.

3.3.5.1.2 Thermal diffusivity and conductivity

Fig. 3.28 shows the plots of thermal diffusivity versus the percentage of expanded graphite at a temperature of 25°C and atmospheric pressure. It can be seen from Fig. 3.28 that thermal diffusivity increases with the increase of the percentage of expanded graphite. The percentage of binder is kept constant at 10% whilst the percentage of expanded graphite changed from 10% to 40% and the percentage of Maxsorb III ranging from 80% to 50%. It should be highlighted that the packing density composite adsorbents also increases with the increases of the percentage of expanded graphite as shown in Fig. 3.28. The thermal conductivity of composite adsorbents at different percentages of expanded graphite is estimated according to the equation (3.10) and the results are depicted in Fig. 3.29. Experimental results show that thermal conductivity increases from 0.15 W m⁻¹ K⁻¹ at a percentage of expanded graphite of 10% and reaches a value of 0.61 W m⁻¹ K⁻¹ at a percentage of expanded graphite of 40%. The thermal conductivity of Maxsorb III powder has been measured at ambient condition using the C-Therm TCi system and found to be 0.066 W m⁻¹ K⁻¹. Therefore, the percentage of improvement in thermal conductivity compared to that of Maxsorb III (powder) ranging from 100% to about 800%. Pino et al.

[133] also observed that equivalent thermal conductivity of 4A-zeolite-based composites increases with the increase of the percentage of graphite. The plot of thermal conductivity of composite adsorbent (50% Maxsorb III, 40% EG, 10% binder) versus the packing density is shown in Fig. 3.30. As can be seen from Fig. 3.30, for the same adsorbent composition, thermal conductivity increases with the increase of packing density. The highest value of thermal conductivity is found to be $0.74 \text{ W m}^{-1} \text{ K}^{-1}$ at a composite packing density of 650 kg m^{-3} which is about 11 times that of Maxsorb III powder. It should be mentioned that larger packing density leads to higher thermal conductivity but lower permeability. Therefore, it is essential to investigate the permeability and estimate the optimum combination between thermal conductivity and permeability of the composite adsorbent.

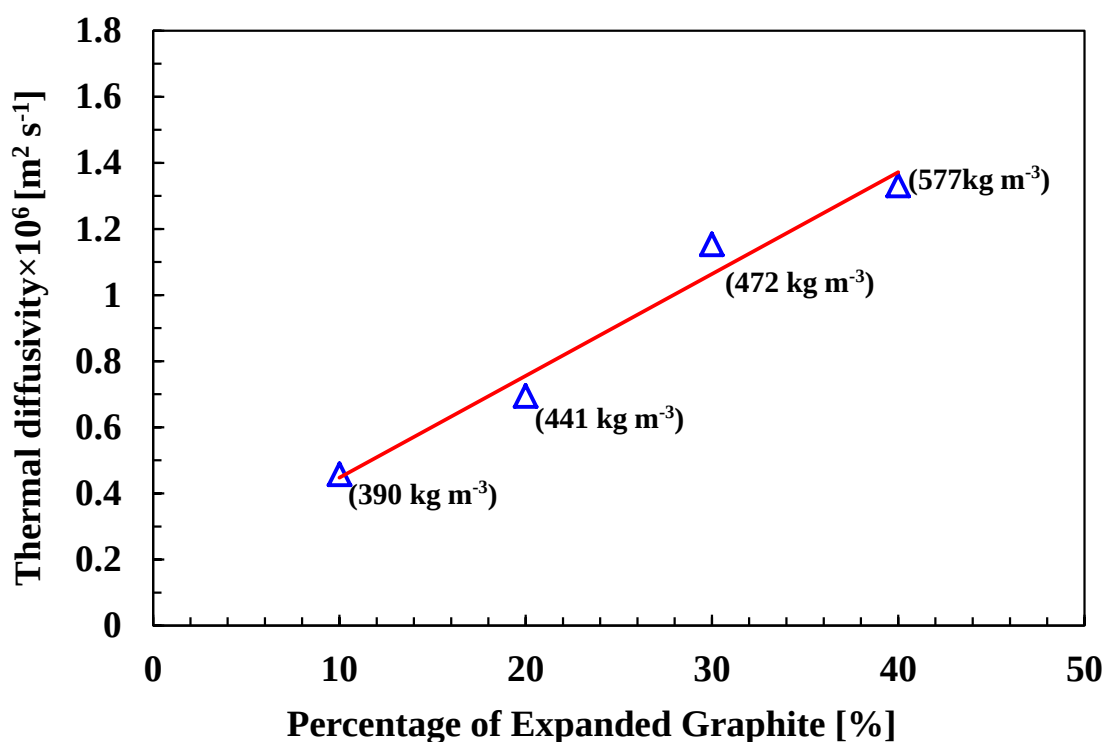


Fig. 3.28 Plots of thermal diffusivity versus the percentage of expanded graphite.

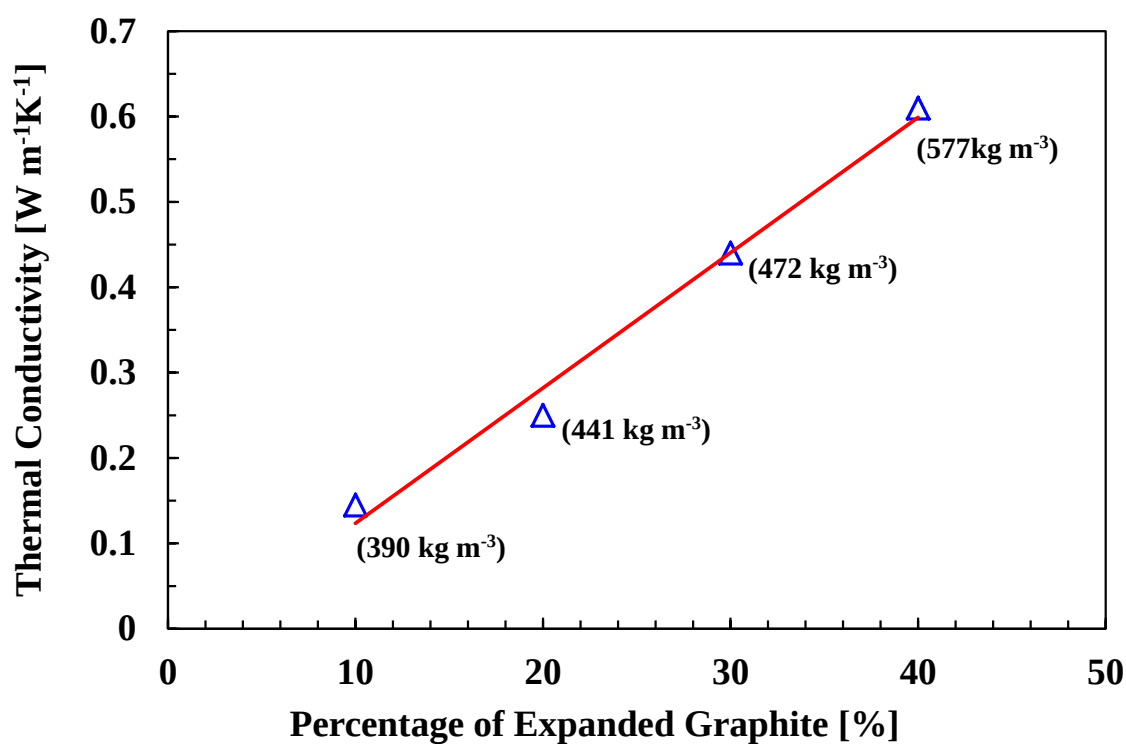


Fig. 3.29 Plots of thermal conductivity versus the percentage of expanded graphite.

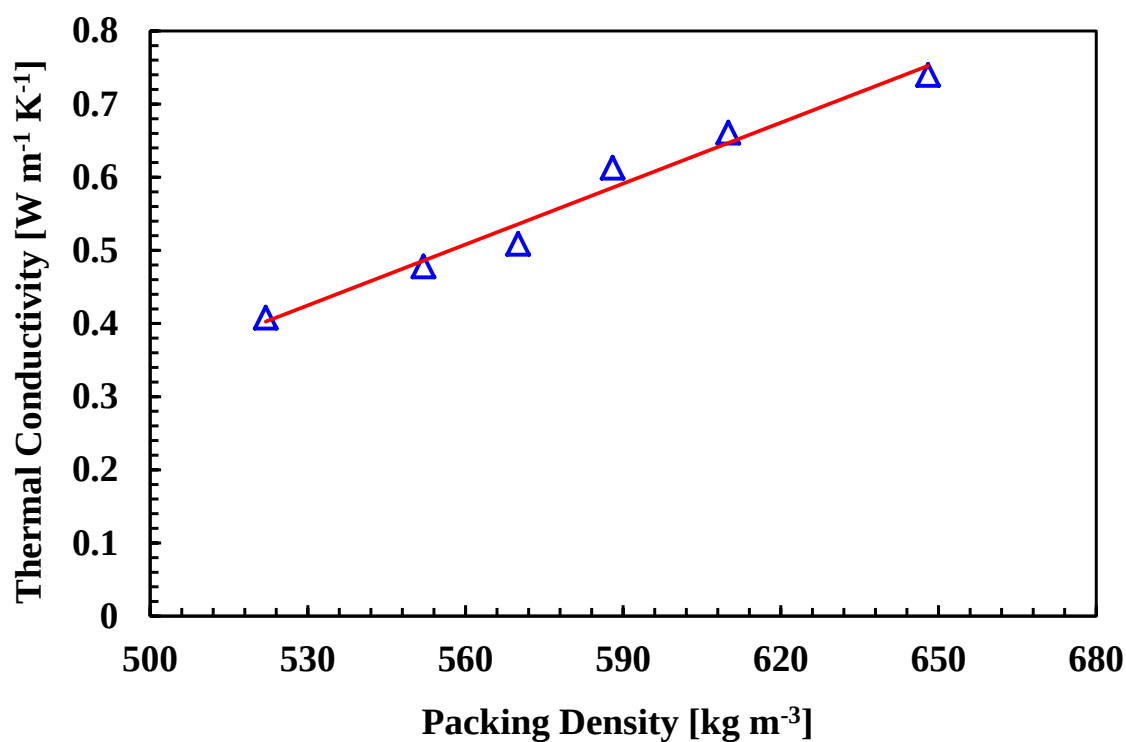


Fig. 3.30 Plots of thermal conductivity of composite A (50% Maxsorb III, 40% EG, 10% binder) versus the packing density.

3.3.5.2 GNP_s contained composites

3.3.5.2.1 Porous properties

Fig. 3.31 shows the N₂ adsorption/desorption isotherm of all synthesized composite 1 to 4 along with parent AC (Maxsorb III). A sharp increase of N₂ adsorption at low relative pressure represents a characteristic feature of microporous materials, which is observed for all studied adsorbents. It can be seen that N₂ adsorption quantity increases with the increase of the percentage of parent Maxsorb III in the composite and no hysteresis has been observed. These are essential characteristics for selecting adsorbent to adsorption cooling or heat pump application. For same composition ratios, the composite 4 shows slightly higher N₂ adsorption uptake compared to composite 2 because of the porous properties of C-grade GNP_s. The surface area of each composite is estimated using Brunauer-Emmett-Teller (BET) model whereas the Non-Local Density Functional Theory (NLDF) is employed to calculate the total pore volume and pore size distribution. The pore size distributions for different composites along with Maxsorb III are presented in Fig. 3.32. The results show that most of the pores of the studied composites lie in between 1 and 3.5 nm, which also ensures that the synthesized composites are microporous. Numerical values of the total BET surface area and total pore volume of the studied composites are summarized in Table 3.12. It is observed that N₂ adsorption data of Maxsorb III is well-matched with literature data [31,44]. Since C750 GNP_s possess higher porous properties than H25, therefore, BET surface area and pore volume of composite 4 is relatively higher than the composite 2, although both composites maintained the same composition ratios. The composite 2 and 3 are prepared using different composition ratios of H25. It is found that the BET surface area and pore volume of composite 2 are higher than composite 3, which follows the higher amount of Maxsorb III in the composite. It can be concluded that additives do not make any significant change in the porous properties. Since Maxsorb III is the main adsorbent in the composite, therefore, BET surface area, pore volume, and pore size distribution (Fig. 3.32) strongly depend on the weight percentage amount of Maxsorb III.

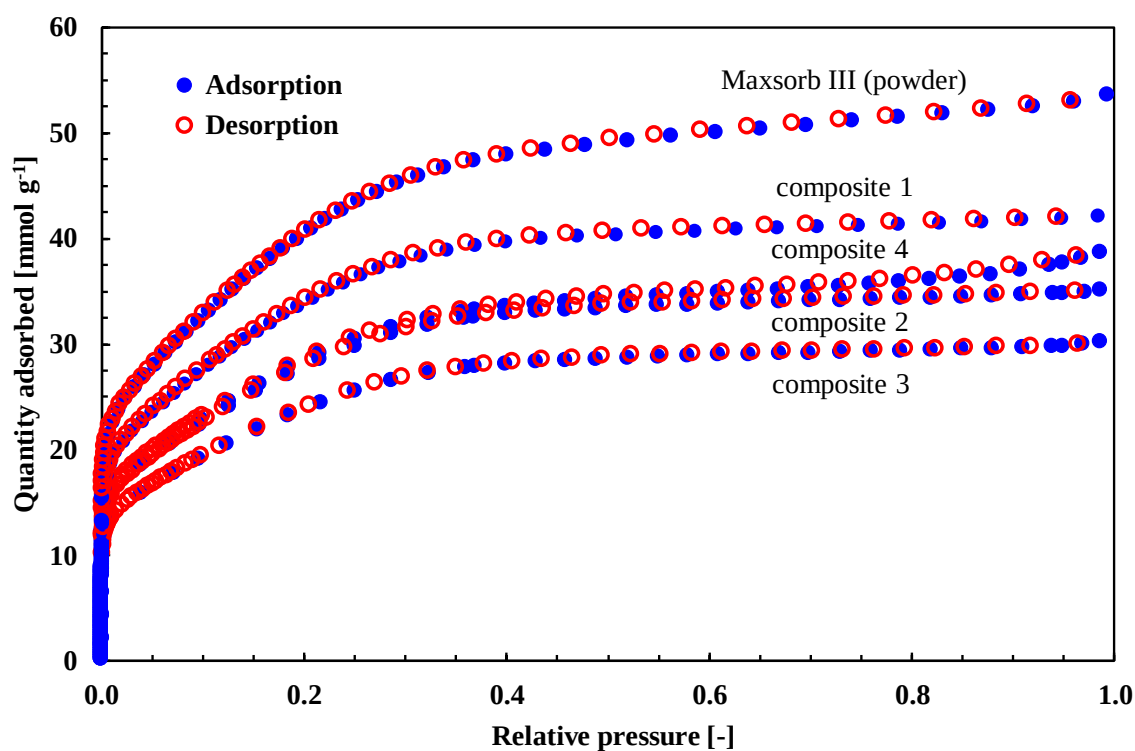


Fig. 3.31 N₂ gas adsorption/desorption isotherm of parent and studied composite adsorbents at 77 K.

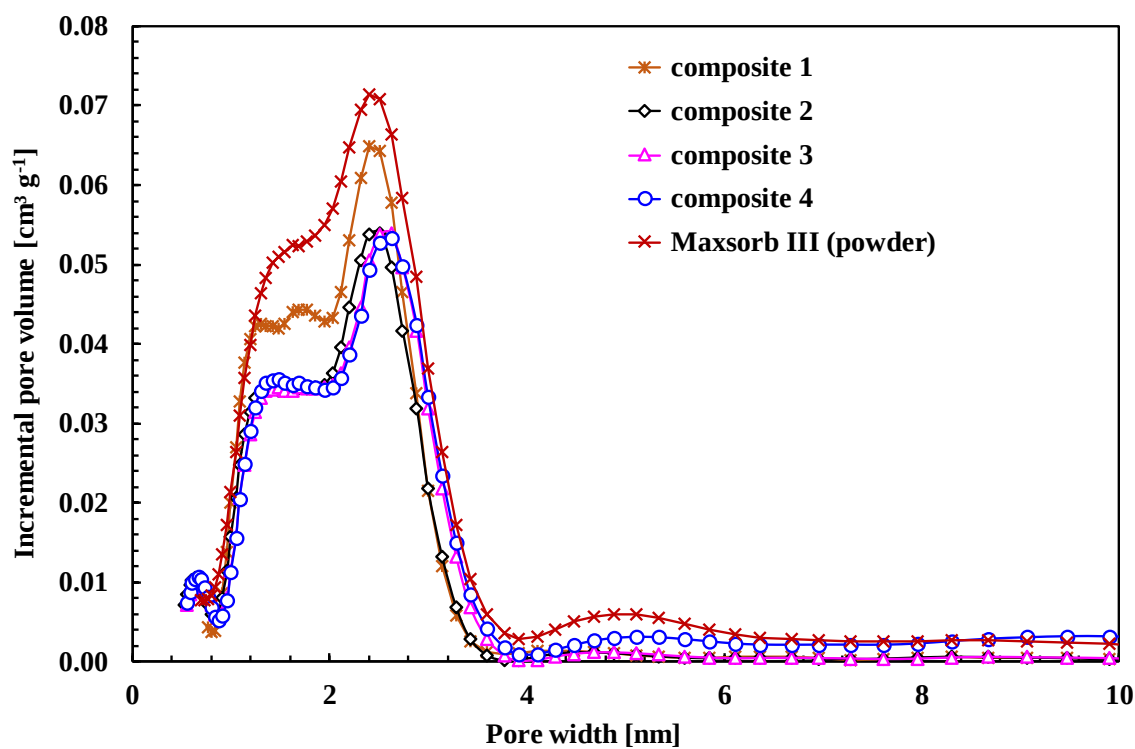


Fig. 3.32 The pore size distribution of parent Maxsorb III and composite.

Table 3.12 BET surface area and pore volume of Maxsorb III and studied composites.

Composite	Total BET Surface area [$\text{m}^2 \text{g}^{-1}$]	Total pore volume [$\text{cm}^3 \text{g}^{-1}$]
composite 1	2730 ± 35	1.339
composite 2	2268 ± 30	1.113
composite 3	1935 ± 20	0.958
composite 4	2310 ± 30	1.233
Maxsorb III	3317 ± 35	1.708

3.3.5.2.2 Thermal diffusivity and conductivity

Thermal diffusivity of studied composites is measured at a temperature ranging from 25 to 100°C. The experiment is repeated five times for each sample and every temperature to check the repeatability and found similar results among the measurement, which is shown in Fig. 3.33. The plots of thermal diffusivity versus temperature for composite 2, 3 and 4 at 25 to 100°C at atmospheric pressure is shown in Fig. 3.33. It can be seen that thermal diffusivity of composite 3 (40 wt% H25) decreases slightly with the increase of temperature whilst composite 2 (20 wt% H25) shows a nominal decrease at higher temperature whereas composite 4 (20 wt% C750) shows constant value over the measured temperatures. It can also be observed that the composite 3 shows very high diffusivity compared to composite 2 and 4 because of a higher amount of H25 graphene into the composite. The high amount of conductive H25 in the composite may establish a conductive network. The thermal conductivity of the composite adsorbent is estimated using the equation (3.10).

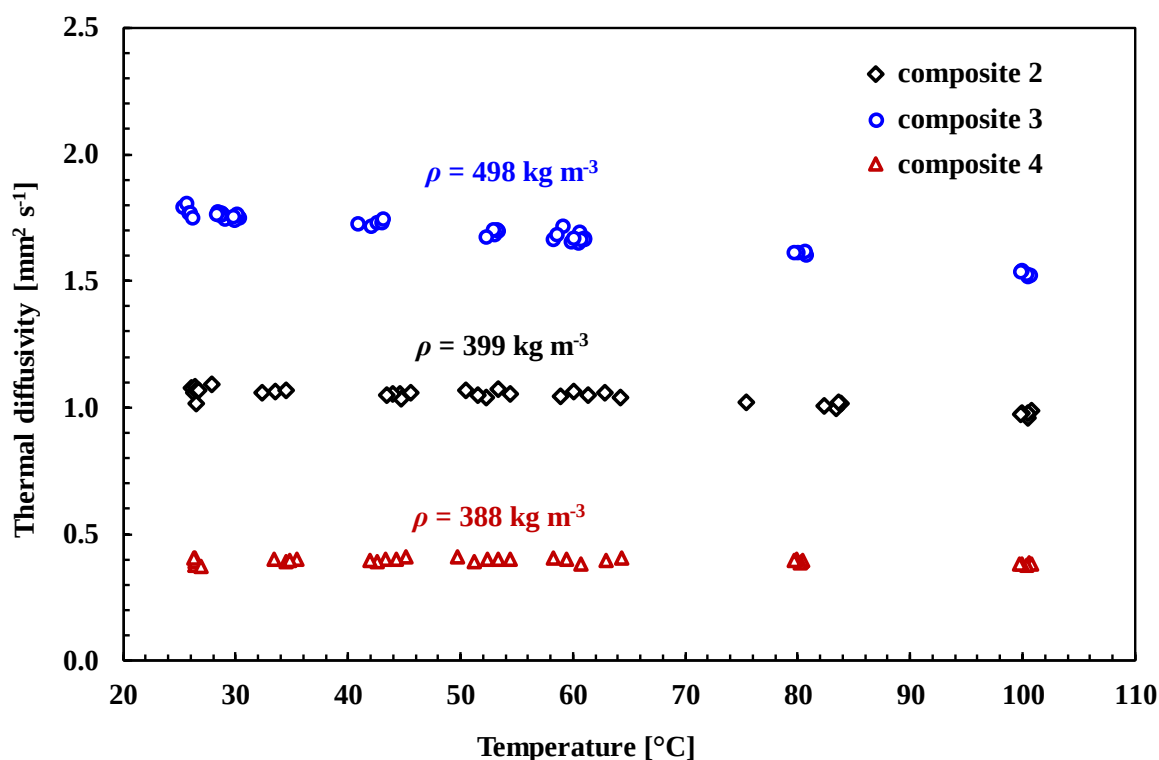


Fig. 3.33 Thermal diffusivity versus temperature for composite 2, 3 and 4.

Thermal conductivity versus temperature for composite 2, 3 and 4 is shown in Fig. 3.34. It is observed that the thermal conductivity are nearly constant for all composites over the temperature ranging from 25 to 100°C. This is due to the inclusion of specific heat capacity in the equation as it is a function of time. From this study, it is found that composite 2 shows higher thermal conductivity followed by composite 2 and 4. The effect of the amount of graphene (H25) content into the composites was also studied. Fig. 3.35 shows the thermal diffusivity versus percentage of graphene (H25) content into the composite. The binder (PVA) percentage is kept constant at 10% whereas the graphene (H25) percentage changed from 20% to 40% and the Maxsorb III percentage is varied from 70% to 50%. It should be mentioned that the packing density of composite adsorbents also increases with the increase of H25 percentage in the composite which is shown in Fig. 3.35 and Fig. 3.36. The bulk density and compressed density of AC powder are 170 kg m⁻³ and 290 kg m⁻³, respectively. However, by adding only 10 wt% binder with Maxsorb III, the density of composite is found to be 316 kg m⁻³ (Fig. 3.34). The introduction of H25 GNPs into the binder and AC, the overall composite packing density increases up to 498 kg m⁻³ at the same compression pressure because H25 particles can strongly attach together. It is

observed that thermal diffusivity, as well as thermal conductivity (Fig. 3.36), increases with the increase of H25 percentage. Thermal conductivity value reaches 0.722 ± 0.007 for composition 50 wt% Maxsorb III + 40 wt% H25 + 10 wt% PVA at packing density 498 kg m^{-3} , which is 994% higher than the Maxsorb III. The thermal conductivity continuously increases the amount of GNPs increased into the composite, which is consistent with the literature [134]. The improvement of thermal properties of composites might be due to the GNPs which provide a conductive surface area with the activated carbon for phonon transport. As the amount of GNPs is increased in the matrix, they are possible to be in closer contact and hence the thermal conductivity increases more quickly. Between H-grade and C-grade GNPs, former one provides a more conductive path through the composite compared to C-grade even at same composition ratios.

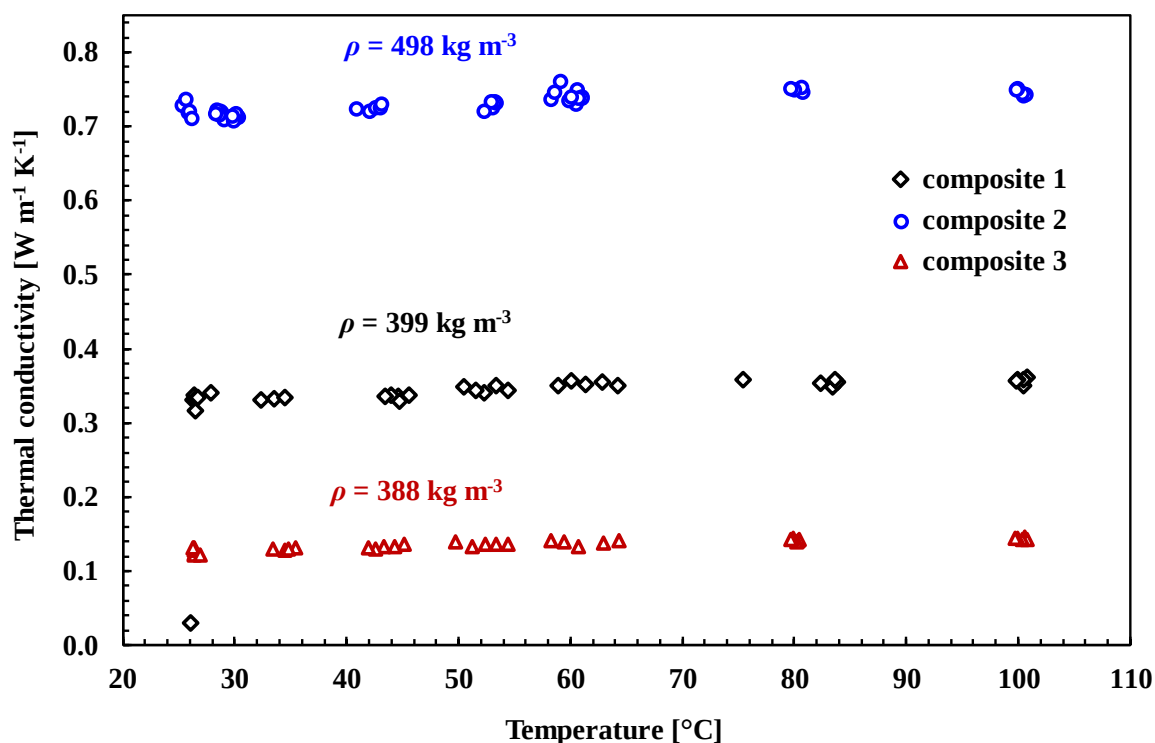


Fig. 3.34 Thermal conductivity versus temperature for composite 1, 2 and 3.

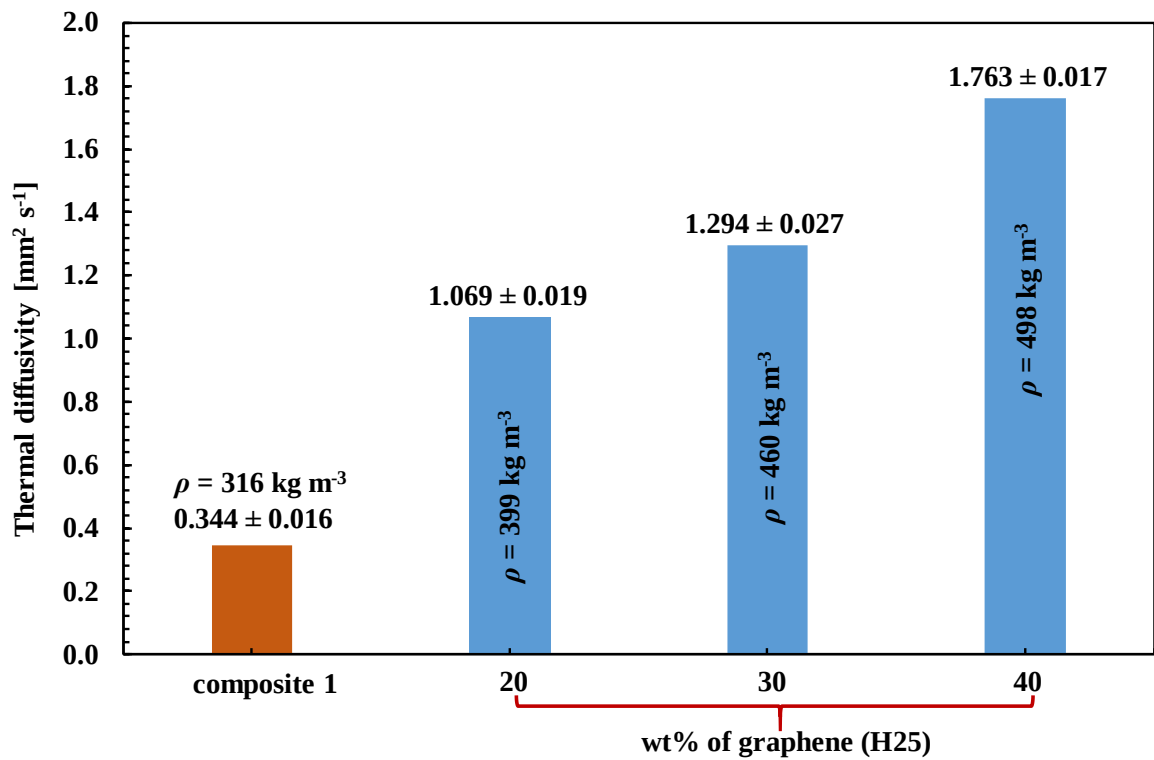


Fig. 3.35 Thermal diffusivities versus percentage of graphene (H25) content into the composite.

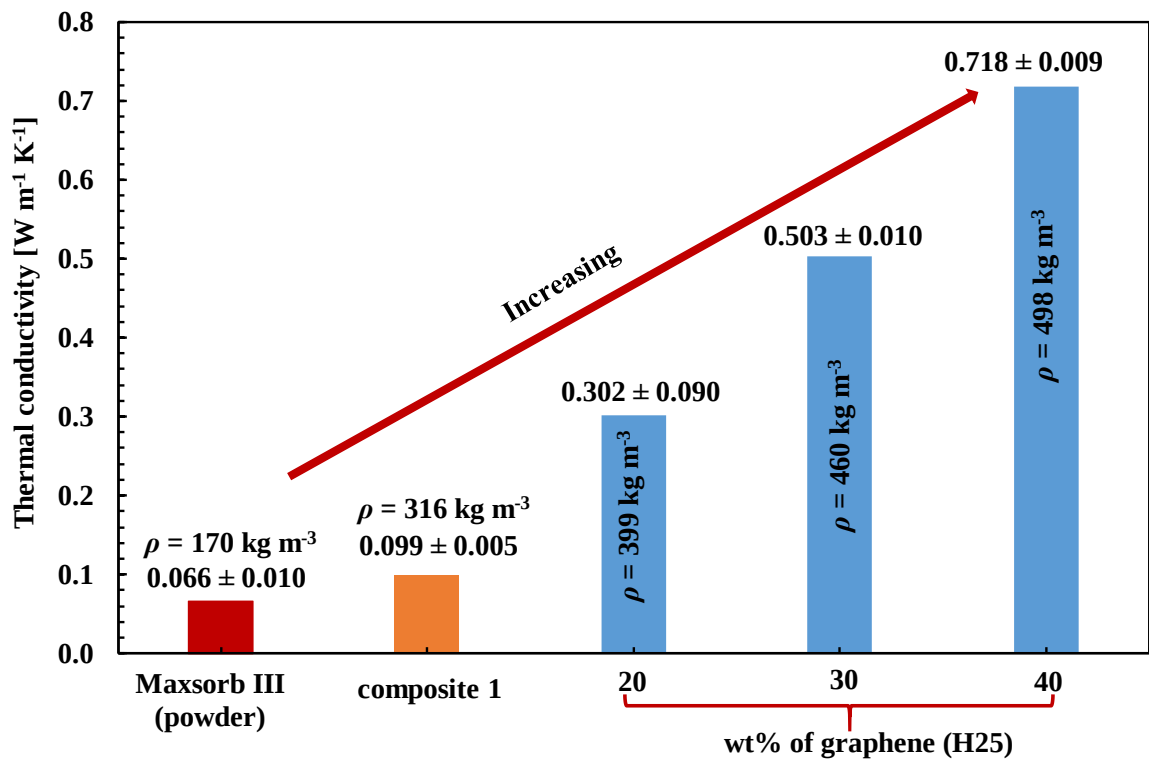


Fig. 3.36 Thermal conductivity versus percentage of graphene (H25) content into the composite.

It is observed that composite contained H25 GNPs possess high thermal diffusivity as well as thermal conductivity compared to C750. Between these two types of graphene, H25 could be promising for enhancing the heat transfer into the adsorber bed. Furthermore, this investigates the thermal diffusivity and thermal conductivity as a function of the packing density of composite 3 (50 wt% Maxsorb III + 40 wt% H25 + 10 wt% PVA). Thermal diffusivity and thermal conductivity of composite 3 versus the packing density are shown in Fig. 3.37 and Fig. 3.38, respectively. As can be seen from both figures, for the same adsorbent composition, thermal diffusivity and conductivity increase with the increase of packing density. It is worth to highlight that the highest value of thermal conductivity is found to be $1.55 \text{ W m}^{-1} \text{ K}^{-1}$ at packing density of 614 kg m^{-3} of composite 3 which is about 23.3 times higher than that of Maxsorb III as can be seen in Fig. 3.39.

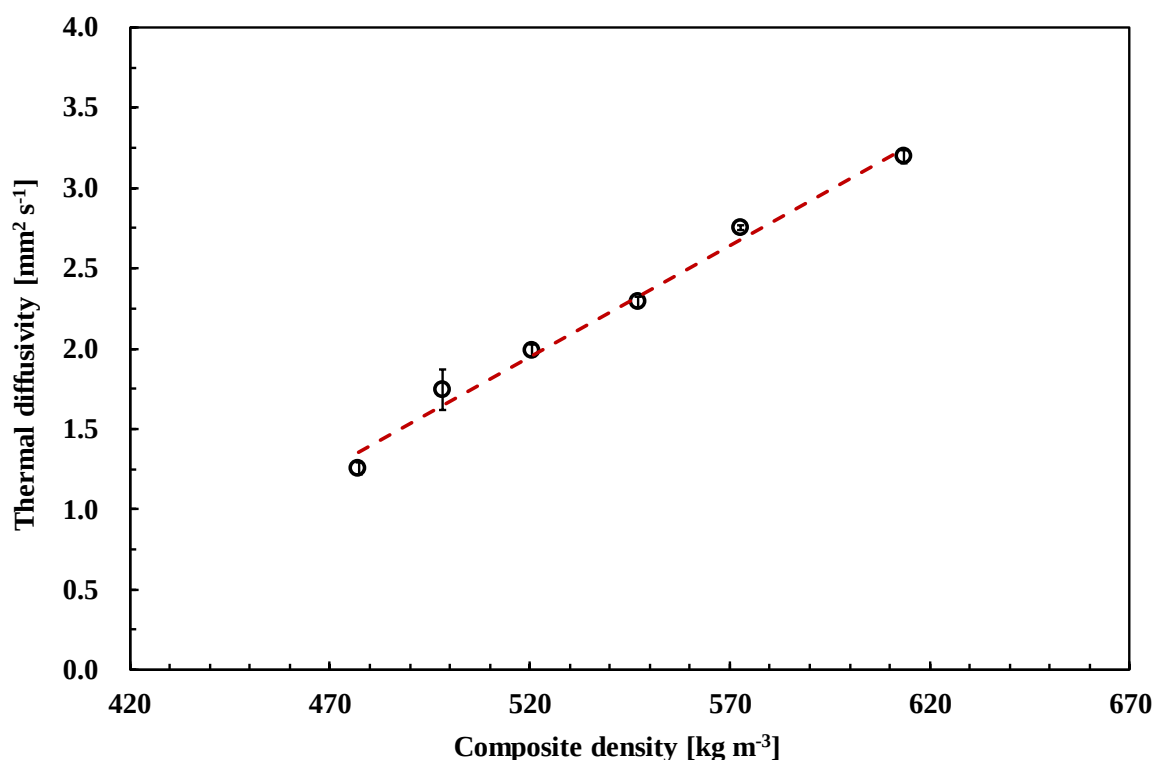


Fig. 3.37 Thermal diffusivities versus packing density of composite 3.

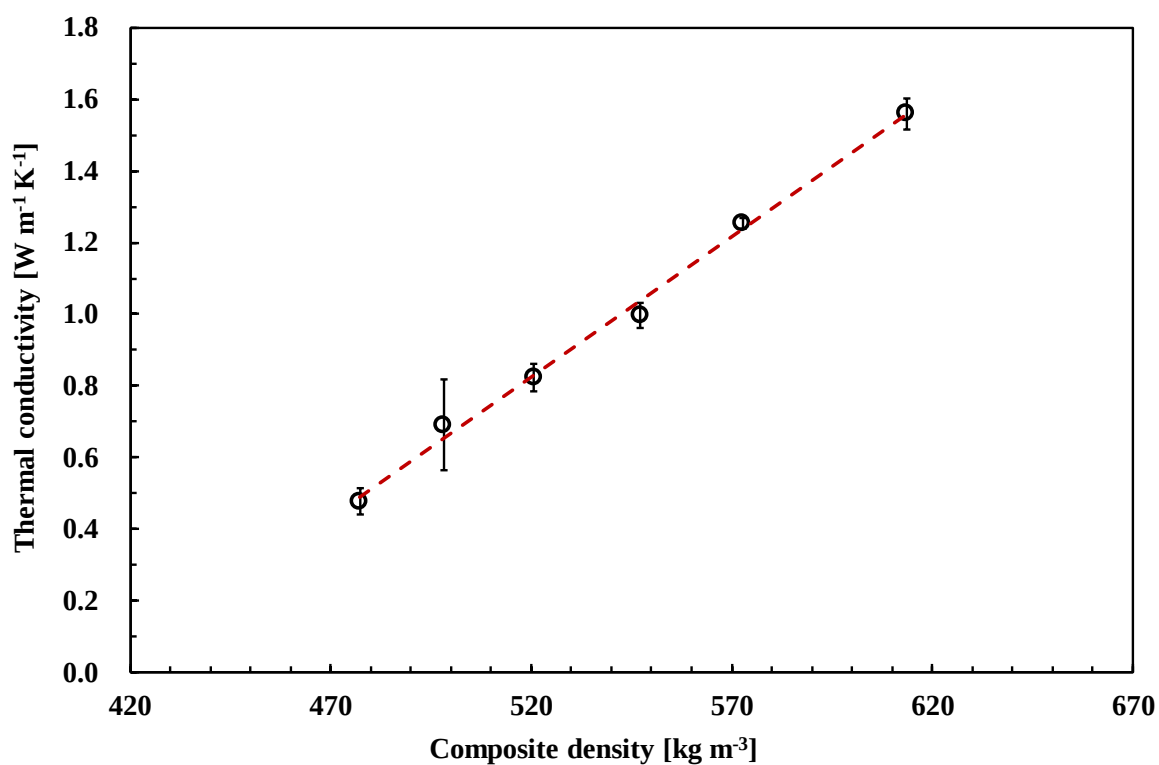


Fig. 3.38 Thermal conductivity versus packing density of composite 3.

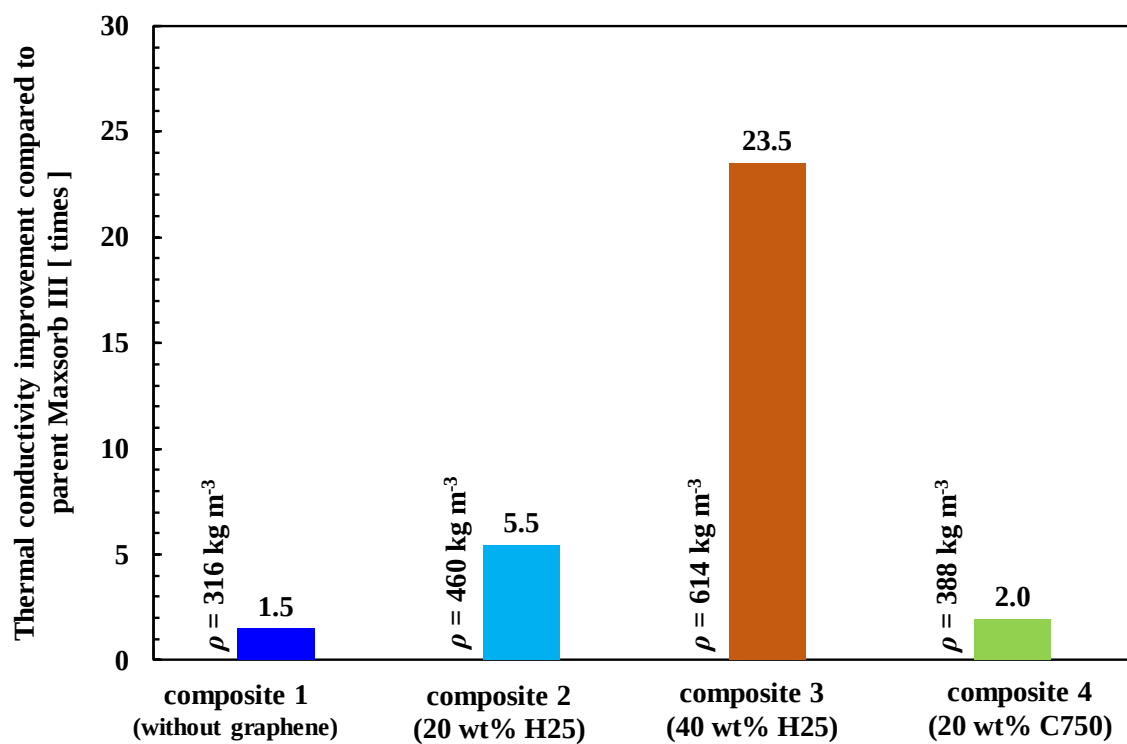


Fig. 3.39 Thermal conductivity improvement compared to Maxsorb III.

3.3.6 Polymerized amino acid based ionic liquid (PAAIL) as a binder

Consolidated composite adsorbents have gained much attention as next generation adsorbents in AHP applications due to some of their salient features such as improved uptake to volume ratio and high thermal conductivity. Numerous synthetic polymer type binders have been investigated for thermal conductivity enhancement such as polyvinyl alcohol (PVA) [46,135], polyvinylpyrrolidone (PVP) [136], expanded graphite [88,91], polytetrafluoroethylene (PTFE) [89] for synthesis composite adsorbents. Nonetheless, such binders have poor affinity for refrigerant vapor [46,135] and pore blockage thereby reducing the uptake potential of such composite adsorbents. Hence, it is imperative to explore improved binders that exhibit not only high thermal conductivity but also are efficient adsorbents. To address these issues, a polymerized ionic liquid (IL) is explored as a potential binder in making consolidated activated carbon composite. Therefore, this section presents the synthesis and characterization of polymerized amino acid based IL named as Poly IL [VBTMA][Ala] (vinyl benzyl trimethyl ammonium alanate) and introduced as a binder for AC (Maxsorb III) based composite.

3.3.6.1 Chemicals

Vinyl benzyl trimethyl ammonium chloride [VBTMA] [Cl] and anion exchange resin (Amberlyst A26 OH form) were procured from Sigma-Aldrich Chemical Co. (St. Louis, MO) and were used as received. The amino acid alanine and solvents ethanol, methanol, and acetonitrile were obtained from Merck, Malaysia. 2, 2'-azobisisobutyronitrile (AIBN) as radical initiator was purchased from R & M, Malaysia.

3.3.6.2 Synthesis of PAAIL

Poly IL [VBTMA][Ala] was synthesized and stored as described elsewhere [94]. Briefly, specified (10g) amount of [VBTMA] [Cl] was mixed with ethanol (200 ml) and stirred few minutes to dissolve it fully. The solution of ethanol and [VBTMA] [Cl] was then passed through the resin [Amberlyst A26 (OH⁻ form)] column slowly. Basically, in this AER method mobile anions (Cl⁻) from [VBTMA] [Cl] + ethanol solution were exchanged with anions that were electrostatically bound to the functional groups (OH⁻) contained within the resin polymer. The resulting vinyl benzyl trimethyl ammonium hydride [VBTMA] [OH] solution was collected and then neutralized the solution with an equimolar amount of alanine at 300 rpm for 24 h. Ethanol and water were removed by

rotary evaporator at water bath temperature 323.15 K with rotation speed of 100 rpm under reduced pressure. After removing those solvents, methanol, and acetonitrile with a ratio of 3:7 were added to the mixture to precipitate out the unreacted alanine, which was separated by filtration. Added solvents were removed again by rotary evaporator to produce the desired amino acid (alanine) IL (AAIL) monomer.

2, 2-azobisisobutyronitrile (AIBN) was used for the polymerization of monomer amino acid (alanine) IL (AAIL). The specified ratio (1:10) of monomer form of IL and AIBN were used for conducting polymerization. Few milliliters of methanol were added and stirred for 24 h at 338.15 K under reflux and inert atmosphere. The resulting polymerized amino (alanine) IL (Poly IL [VBTMA][Ala]) was dried in vacuum oven at 353.15 K and further dried using an air oven at 373.15 K [94]. The synthesis path of PAAIL is shown in Fig. 3.40.

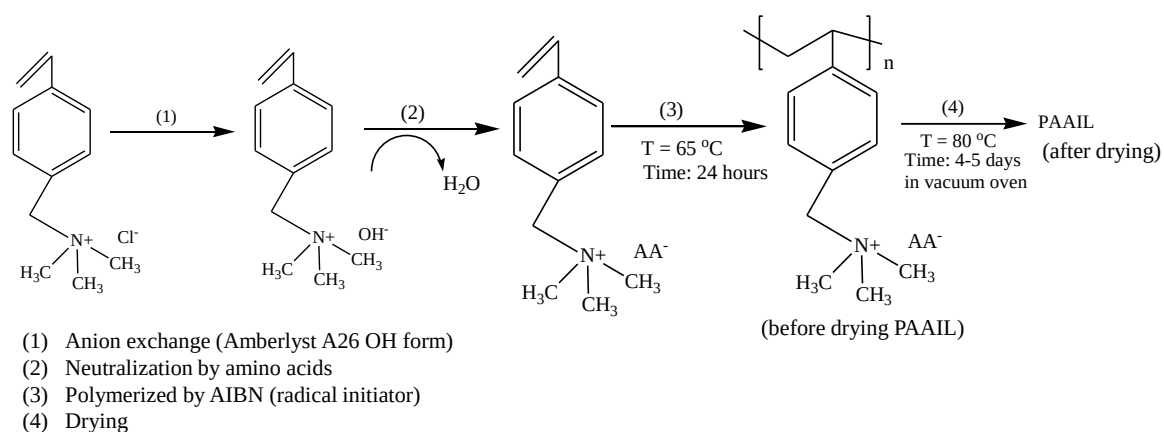
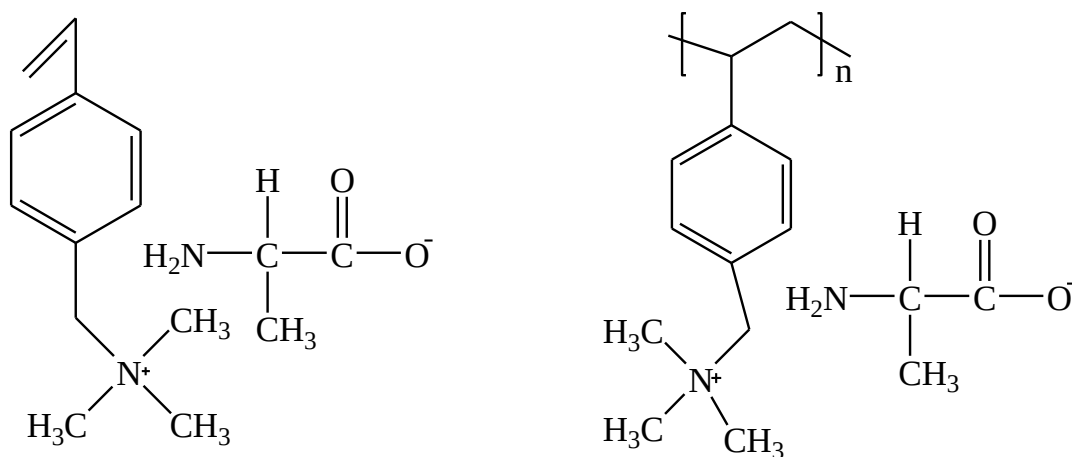


Fig. 3.40 Synthesis route of polymerized AAIL (PAAIL).

3.3.6.3 Characteristics of polymerized AAIL (PAAIL)

Molecular structures of the monomer and polymer forms of amino acid based ionic liquid ([VBTMA][Ala]) are shown in Fig. 3.41. In this study, polymerized amino acid IL (PAAIL) chemical named as Poly IL [vinylbenzyltrimethyl ammonium][alanate] has been used as a binder for composite synthesis as the amine-functionalized polymerized IL works as a good adsorbent. To confirm the structure of the synthesized PAAIL, ^1H -NMR has been conducted. ^1H -NMR spectrum for [VBTMA][Ala] and Poly IL [VBTMA][Ala] are shown in Fig. 3.42 and Fig. 3.43, respectively whilst details of the spectrum are provided in the experimental section. According to ^1H -NMR, the vinyl protons in [VBTMA][Ala] have seen at around 5 to 7 ppm (Fig. 3.42), which has been shifted to upfield 1.5 to 2.2

ppm in the Poly IL [VBTMA][Ala] (Fig. 3.43). This can be attributed to a long alkyl group in the polymer ILs. These results clearly indicate that the vinyl compounds in the monomer are successfully polymerized. In addition, all peaks of the monomer became broad after polymerization, a well-known phenomenon in polymer technology.



Monomer form of [VBTMA][Ala]

Polymer form of [VBTMA][Ala]

Fig. 3.41 Molecular structures of the monomer and polymer forms of amino acid based ionic liquid.

Differential scanning calorimetry (DSC) result shows that the glass transition temperature (T_g) of Poly IL [VBTMA][Ala] is 244.44 K. Thermogravimetric analyzer (TGA) result shows the degradation temperature (T_d) of Poly IL [VBTMA][Ala] is 458.3 K. For composite synthesis, the temperature of 393.15K has been applied to evaporate compounds like water and ethanol. In addition, AHP systems are usually driven using heat sources less than 373.15 K [10,28,97,137] whilst the synthesized polymerized IL is thermally stable up to 458.3 K. Thus, the synthesized Poly IL [VBTMA][Ala] can be employed as a potential binding material in making composite adsorbent for AHP applications.

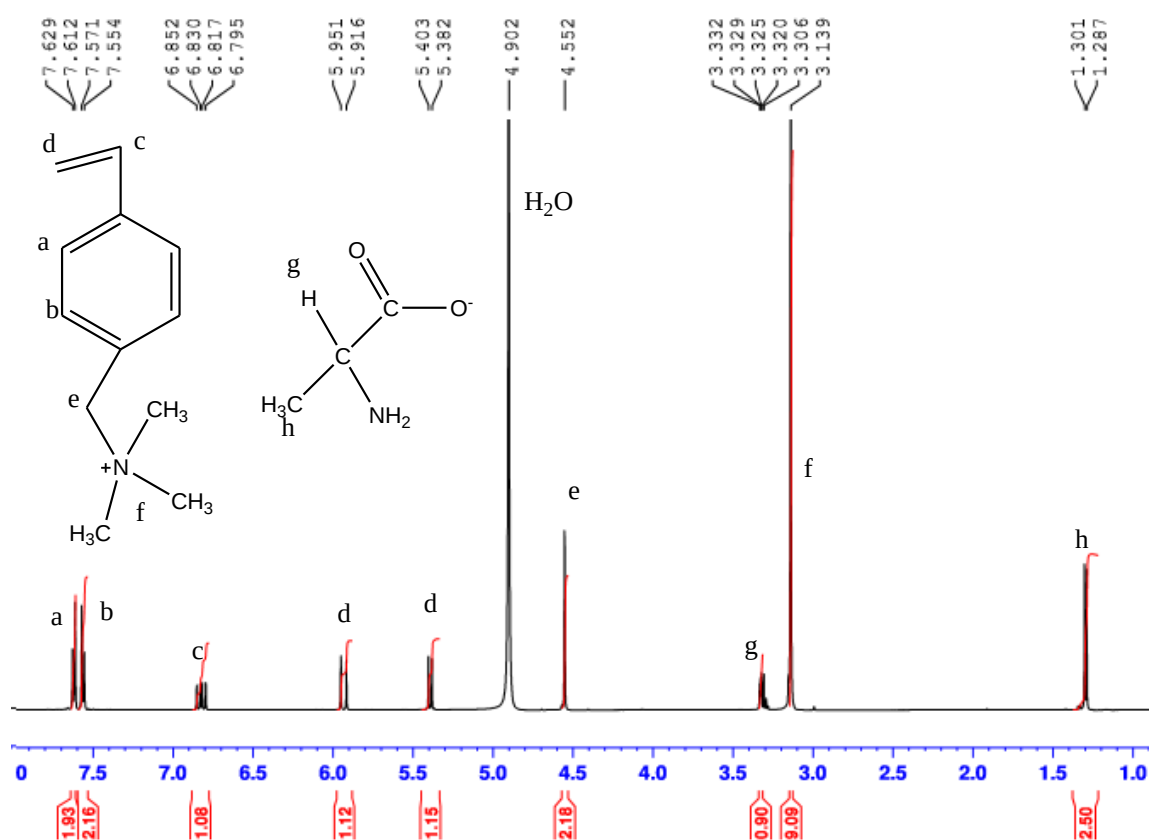


Fig. 3.42 ^1H -NMR spectrum of monomer form of [VBTMA][Ala]. The numbers below each signal are the integral values and are used to quantify the *proton* in [VBTMA][Ala].

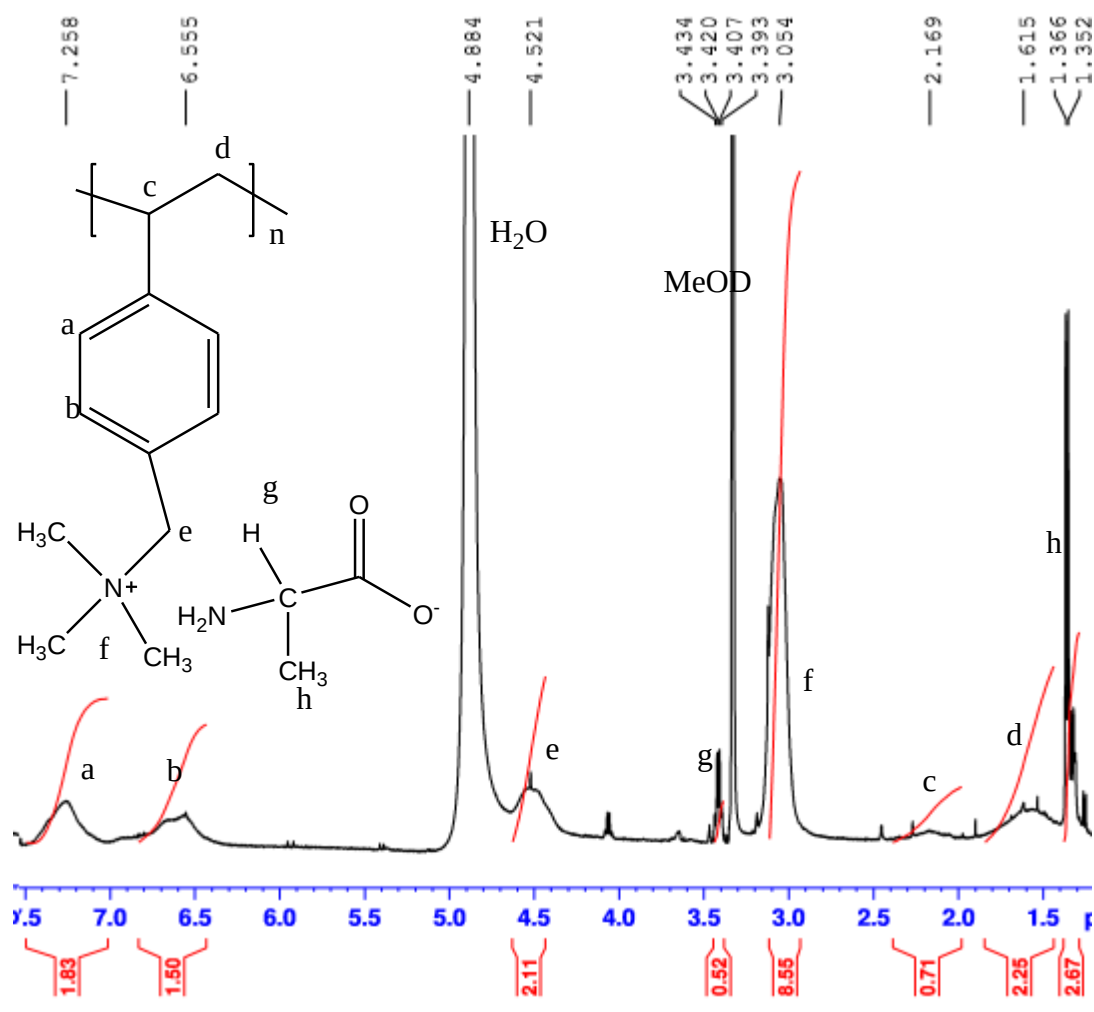


Fig. 3.43 ^1H -NMR spectrum of polymer form of [VBTMA][Ala]. The numbers below each signal are the integral values and are used to quantify the proton in Poly IL [VBTMA][Ala].

3.3.6.4 Poly IL [VBTMA][Ala] as a binder for AC composite

Fig. 3.44 represents the schematic diagram of composite synthesis process of using Poly IL [VBTMA][Ala]. The process can be elucidated as follows [46,135]; firstly, activated carbon namely Maxsorb III were dried in the oven at a temperature of 393.15K for about 6 h to remove the moisture content for minimizing the mass error. Subsequently, Poly IL [VBTMA][Ala] was kept into ethanol solvent where it turns into a viscous solution. Maxsorb III and Poly IL [VBTMA][Ala] were then mixed and the mixture was compressed using a pressing machine. Finally, the composite adsorbent sample was dried in an air oven at 393.15 K for several hours. The mass ratio in the prepared composite was 90 wt% Maxsorb III and 10 wt% Poly IL [VBTMA][Ala]. In this study, the composite

using Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) will be named as Composite A whilst Maxsorb III (90 wt%) + PVA (Polyvinyl alcohol) (10 wt%) as Composite B.

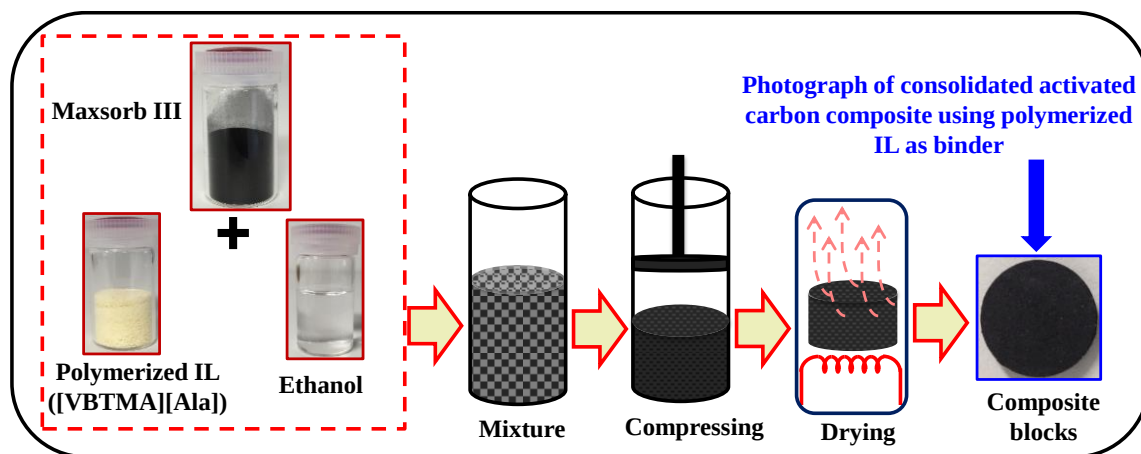


Fig. 3.44 Schematic diagram of the composite synthesis process.

As mentioned in the many literature [96,138–143], one of the applications of the polymerized ionic liquid synthesized is in capturing CO₂. Preliminary CO₂ adsorption characteristics were measured for the present consolidated composite with polymerized IL as a binder (Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)) and volumetric adsorption uptake is shown in Fig. 3.45. Significant enhancement in the volumetric uptake of CO₂ adsorption was observed, as indicated in the literature [94,95,144]. Therefore, improvement of CO₂ uptake onto composite containing polymerized IL as binder encouraged to perform adsorption of ethanol as a promising refrigerant for AHP application. Details on the ethanol adsorption onto the same composite with polymerized IL as the binder will be discussed in chapter 4.

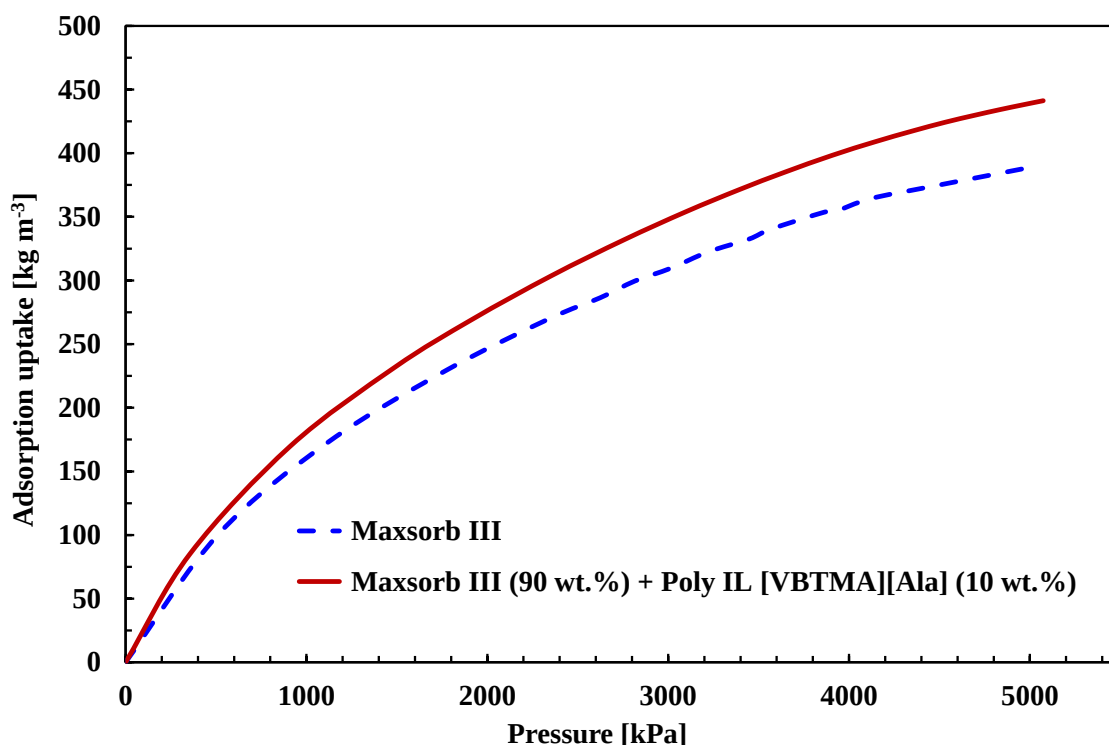


Fig. 3.45 Comparison of volumetric adsorption uptake of CO₂ onto Maxsorb III and composite with PIL as a binder at adsorption temperature 303.15 K.

3.3.6.5 Characteristics of composites

Porous characteristics, such as surface area, pore volume and pore size distribution of the composite A and composite B have been calculated from N₂ gas adsorption/desorption isotherm at 77 K. The N₂ gas adsorption/desorption isotherm of the developed composites is shown in Fig. 3.46. At very low relative pressure, a steep increase of nitrogen adsorption amount can be observed, which represents a characteristic feature of microporous materials. It is observed that the composites exhibit no noticeable hysteresis on the N₂ adsorption and desorption isotherms, indicating the absence of mesopores. Such characteristics are important for the AHP application. The Brunauer-Emmett-Teller (BET) method with multi-point surface area analysis is adopted to calculate the total surface area of both adsorbents. The specific surface area and pore volume of the composite with polymerized IL (composite A) are about 3040 m² g⁻¹ and 1.59 cm³ g⁻¹, respectively. It is observed that surface area and pore volume of composite A are 11% and 18% higher than that of composite B, respectively. This observed phenomenon is due to the polymerized ionic liquids having an affinity towards vapor molecules [94,145,146],

unlike PVA which does not show any affinity. Pore size distributions (PSD) as predicted by Non-Local Density Functional Theory (NLDFT) method for both adsorbents are shown in Fig. 3.47. The numerical value of porous properties of both composites has been furnished in Table 3.13.

The thermal conductivity of Maxsorb III is about $0.066 \text{ W m}^{-1} \text{ K}^{-1}$ at ambient condition [46]. Fig. 3.48 shows the comparison of thermal conductivity of among Maxsorb III (90 wt%) + PVA (Polyvinyl alcohol) (10 wt%), Maxsorb III, and Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%). It is found that Maxsorb III (90 wt%) + PVA (10 wt%) possesses thermal conductivity $0.099 \text{ W m}^{-1} \text{ K}^{-1}$ which is about 50% improvement as compared to Maxsorb III powder. However, the thermal conductivity of composite A (Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)) is $0.122 \text{ W m}^{-1} \text{ K}^{-1}$ which is about 85% higher than parent adsorbent (Maxsorb III). Therefore, it is important to mention here that consolidated composite with polymerized IL as a binder shows higher thermal conductivity than polyvinyl alcohol as a binder.

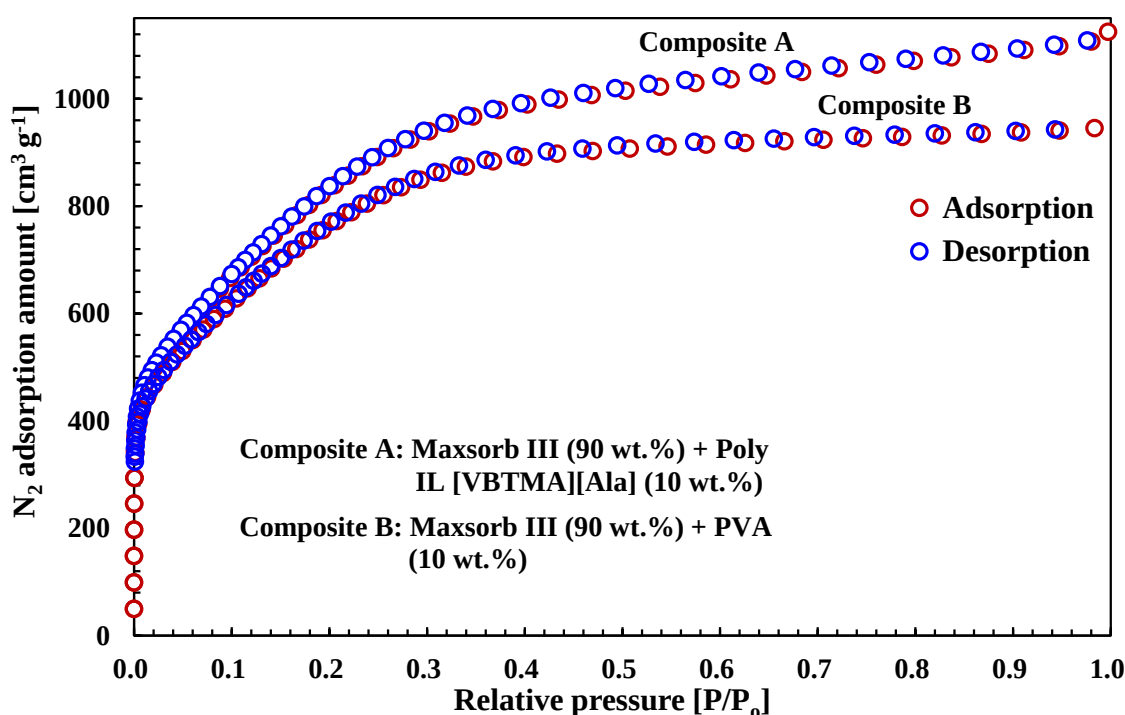


Fig. 3.46 Comparison of N_2 gas adsorption/desorption between Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) and Maxsorb III (90 wt%) + PVA (10 wt%) at 77 K.

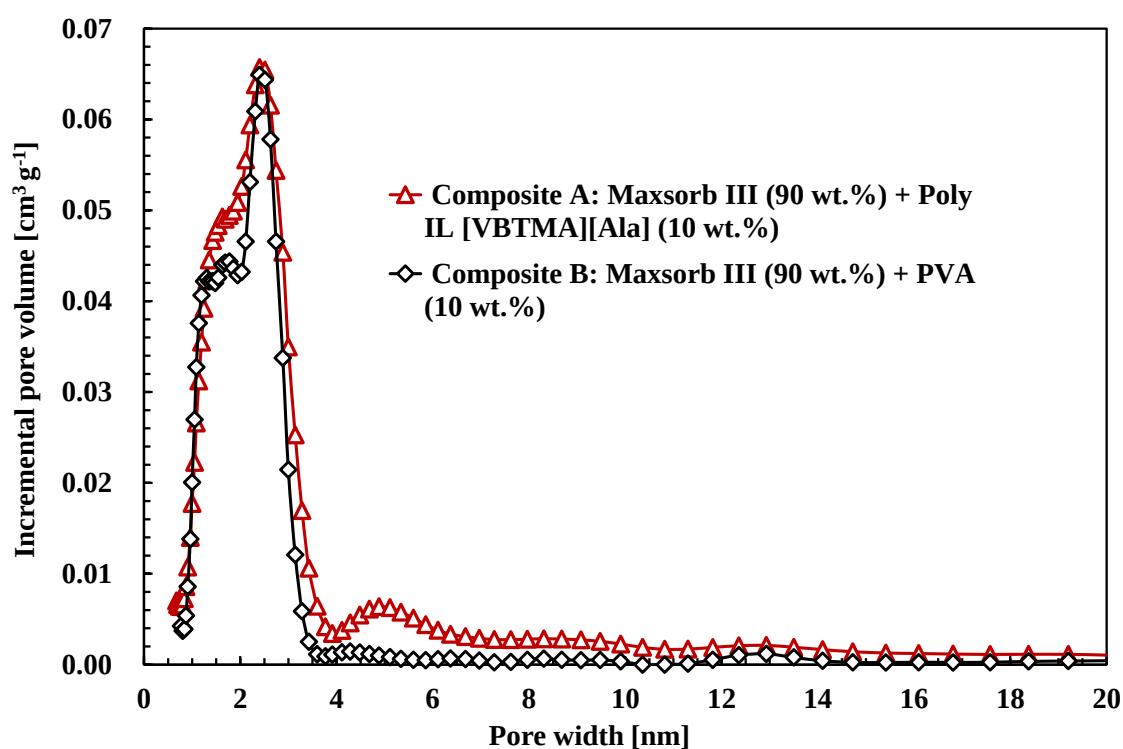


Fig. 3.47 Pore size distribution of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) and Maxsorb III (90 wt%) + PVA (10 wt%).

Table 3.13 Porous properties and thermal conductivity of the studied composite.

Adsorbent	Total surface area [m ² g ⁻¹]	Total pore volume [cm ³ g ⁻¹]	Thermal conductivity [W m ⁻¹ K ⁻¹]
Composite A: Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)	3040 ± 32	1.59	0.122
Composite B: Maxsorb III (90 wt%) + PVA (10 wt%)	2730 ± 35	1.34	0.099

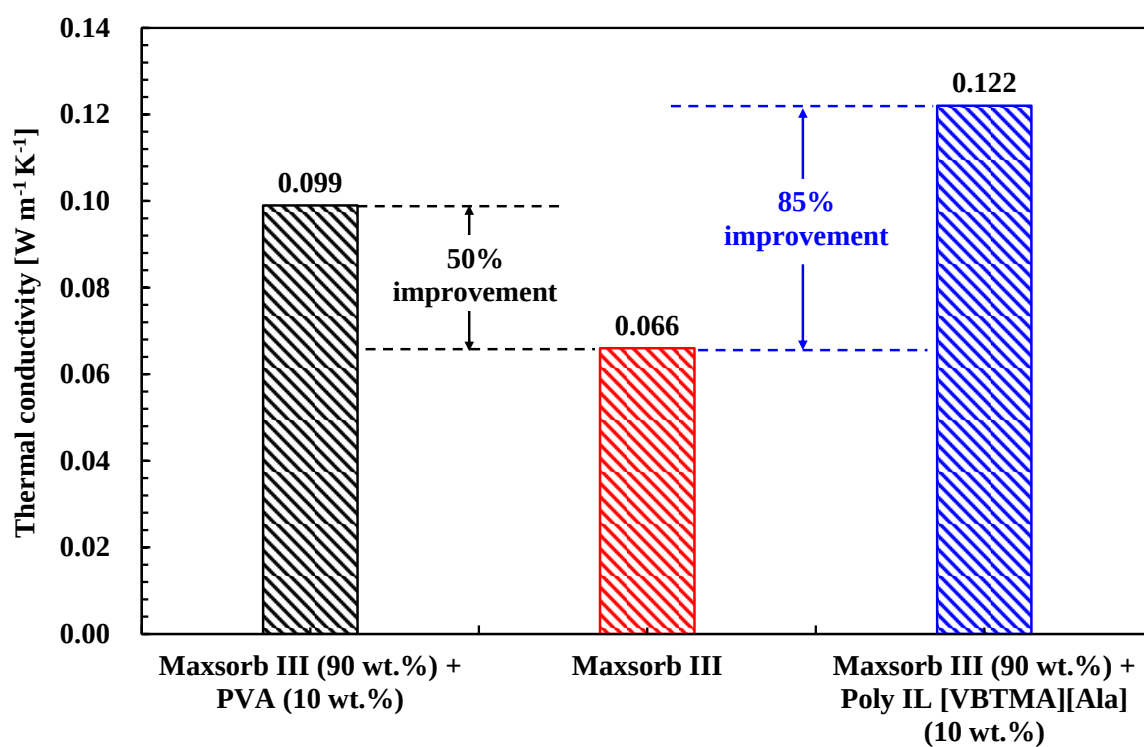


Fig. 3.48 Comparison of thermal conductivity of among Maxsorb III, Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%), and Maxsorb III (90 wt%) + PVA (10 wt%).

3.4 Conclusions

Biomass-derived ACs: In this study, activated carbons with high porous properties are synthesized from two waste biomasses, namely, waste palm trunk and mangrove. The study shows that carbonization temperature at 500 and 600°C is the optimum condition to obtain the activated carbons with high carbon and yield content. This temperature is enough to remove almost 100% of all volatile matters and tars. It is found that drying WPT and mangrove gives a yield of 30 wt% or more in the carbonization process at temperature 500°C at a heating rate of 10°C/min for 1 hour. By KOH activation, biomass-derived activated carbons produced 20 to 50 wt% of yield. Particularly, mangrove-derived ACs produced higher yield compared to WPT. The N₂ isotherms show that activated carbons obtained from WPT and mangrove, by KOH activation technique, have a high degree of porosity and located mainly in the micro size of pores. ACs with a surface area between 1400-3000 m² g⁻¹ having 0.65 to 2.87 cm³ g⁻¹ pore volume is successfully prepared from both biomasses. It is worthy to mention that the highest surface area and pore volume of WPT-derived ACs are found to be 2927 m² g⁻¹ (WC600A900K6) and 2.87 cm³ g⁻¹ (WC500A900K6) whilst 2924 m² g⁻¹ (MC600A900K6) and 2.68 cm³ g⁻¹ (MC500A900K6) are for M-derived AC. Generally, increasing the activation temperature and mass ratio of KOH/carbon can enhance the porous properties. The micropore widening of the AC proceeds when increasing the activation temperature and mass ratio of KOH/carbon. It is found that all porous properties are saturated at a certain condition and decreases at the severe condition. Moreover, at the same time activation yield also decreases at higher temperature and KOH ratio. It can be concluded that carbonization at 500 and 600°C, activation at 900°C, and six times KOH create highest surface area and pore volume ACs derived from both kinds of biomasses. Therefore, WC500A900K6, WC600A900K6, MC500A900K6, and MC600A900K6 can be selected as a promising adsorbent among all the synthesized ACs for AHP applications. Experimental results show that thermal conductivity values vary from 0.054 to 0.041 W m⁻¹ K⁻¹ for WPT-derived ACs whilst 0.061 to 0.045 W m⁻¹ K⁻¹ are for M-derived ACs. Finally, it can be concluded that WPT and mangrove are suitable precursor materials for the production of highly porous activated carbons and could be very promising adsorbents for adsorption heat pump applications.

EG contained AC composites: Consolidated composite adsorbents which are combinations of Maxsorb III, expanded graphite (EC500), and PVA binder has been

developed. Porous properties of the synthesized consolidated composite adsorbents have been investigated experimentally from nitrogen adsorption isotherm and show high porous properties with micropore. It is found EG and binder does not block the pores. Therefore, the porous properties strongly depend on the percentage of parent AC (Maxsorb III). Experimental results also show that the thermal diffusivity and conductivity of composite adsorbents increases with the increasing percentage of expanded graphite. It should be highlighted that the packing density composite adsorbents also increases with the increases in the percentage of expanded graphite. Experimental results show that thermal conductivity increases from $0.15 \text{ W m}^{-1} \text{ K}^{-1}$ at a percentage of expanded graphite of 10% and reaches a value of $0.61 \text{ W m}^{-1} \text{ K}^{-1}$ at a percentage of expanded graphite of 40%. At the same adsorbent composition ratios (50% Maxsorb III, 40% EG, 10% binder), thermal conductivity increases with the increase of packing density. Among the tested samples, the highest value of thermal conductivity is found to be $0.74 \text{ W m}^{-1} \text{ K}^{-1}$ at a composite packing density of 650 kg m^{-3} , which is about 11 times that of Maxsorb III powder. It should be mentioned that larger packing density leads to higher thermal conductivity but lower permeability. Therefore, it is important to investigate the permeability and estimate the optimum combination between thermal conductivity and permeability of the composite adsorbent.

GNPs contained AC composites: A series of consolidated AC composites are synthesized employing graphene nanoplatelets (GNPs) as a thermal conductivity enhancer and polyvinyl alcohol (PVA) as a binder. Porous properties are calculated from the N_2 adsorption data using BET and NLDFT methods. It is found that studied composites are microporous and their porous properties mainly depend on the composition ratio of AC. With the same composition ratios, composite 4 shows higher BET surface and pore volume compared to composite 2 because porous properties of C750 is higher than H25. The composite without GNPs shows just only 1.5 times higher thermal conductivity than the AC powder. However, thermal diffusivity, as well as thermal conductivity increases by introducing GNPs into the AC and binder. Experimental results show that H-grade GNPs is superior for enhancing the thermal conductivity of AC based composite compared to C-grade. The adding of both the GNPs in the composite increases the packing density. It is also observed that the thermal conductivity increases with the increasing of packing density and the highest thermal conductivity are found $1.55 \text{ W m}^{-1} \text{ K}^{-1}$ for composite 3 at packing density of 614 kg m^{-3} , which is about 23.5 times higher than AC powder.

Composite using PIL binder: The use of polymerized IL as a potential binder in the synthesis of consolidated activated carbon composite for AHP applications has been explored. Maxsorb III has been consolidated using polymerized IL vinylbenzyltrimethyl ammonium alanate [VBTMA][Ala] (10 wt%) as a composite material. Porous characteristics investigation shows that the specific surface area and pore volume of the consolidated composite using polymerized IL as a binder are $3040 \text{ m}^2 \text{ g}^{-1}$ and $1.59 \text{ cm}^3 \text{ g}^{-1}$, respectively. It is noted that the surface area and pore volume of PIL composite increased by more than 11% and 18%, respectively, as compared to the PVA composite. In addition, the thermal conductivity of PIL composite exhibits $0.122 \text{ W m}^{-1} \text{ K}^{-1}$ which is about 85% higher than that of Maxsorb III. Therefore, consolidated activated carbon composite using polymerized IL as a binder shows high porous properties and remarkably high thermal conductivity which are desirable properties of the adsorbent for developed next generation AHP systems.

Chapter 4

Application to low pressure adsorption systems

The adsorbent is one of the key elements in the adsorption heat pump system. In chapter 3, the author presented synthesis and characteristics of a series of functionally activated carbons from renewable and waste biomasses, and composite adsorbents using expanded graphite (EG) and graphene nanoplatelets (GNPs) as a thermal conductivity enhancer. The author also introduced polymerized amino acid-based ionic liquid (PAAIL) as a binder for the first time to synthesis composite adsorbent. Synthesized adsorbents showed superior porous properties and enhanced thermal conductivity compared to existing activated carbon-based adsorbents. Therefore, the preliminary characteristics results of developed adsorbents showed promising for adsorption heat pump applications. Consequently, in this chapter, the author has been investigated the feasibility of ethanol adsorption characteristics (equilibrium uptake and instantaneous uptake) on developed adsorbents at a wide range of adsorption temperature and pressure. The gravimetric method based magnetic suspension adsorption measurement unit and experimental setup of measuring the liquid refrigerant level at evaporator side are employed to measure the ethanol uptake. To investigate the adsorption behavior, the experimental data are further analyzed using various adsorption isotherm and kinetics models.

4.1 Introduction

Thermally powered AHP systems seem to be a promising alternative to conventional vapor compression cycles. The main advantages of these systems are; (i) they can be driven using low temperature heat source below 100°C, (ii) almost no electricity is needed [1]. In addition, naturally available fluid such ethanol, methanol, and water can be used as a refrigerant. Among those refrigerants, numerous studies have been focused on ethanol as a refrigerant on metal-organic frameworks based system [55,147], adsorption cooling and desalination system [10], phenol resin-derived activated carbon based cooling systems [104], activated carbon (Maxsorb III) based heating and cooling system [15,16],

activated carbon fiber based system [54,75,76]. Above-mentioned studies showed that ethanol is promising for activated carbon based adsorbent. Table 4.1 shows the thermophysical properties of ethanol.

Table 4.1 Thermo-physical properties of ethanol.

Chemical formula	C ₂ H ₆ O
Molar mass	46.07 g/mol
Appearance	Colorless liquid
Density	0.789 g/cm ³ (at 20°C)
Melting point	−114 °C (−173 °F; 159 K)
Boiling point	78.37 °C (173.07 °F; 351.52 K)
Critical point	514 K (241 °C), 63 bar
Vapor pressure	5.95 kPa (at 20 °C)
Enthalpy change of vaporization	38.56 kJ/mol

In this chapter, the adsorption characteristics (isotherm and kinetics) of environmentally benign ethanol onto; i) waste palm trunk (WC600A900K6) and mangrove (MC600A900K6)-derived ACs; ii) expanded graphite (EG) contained composites; iii) graphene nanoplatelets (GNPs) contained composites; and iv) composite using polymerized amino acid-based ionic liquid (PAAIL) as a binder have been investigated using liquid level measurement experimental setup and thermo-gravimetric analyzer (TGA) unit. Various adsorption isotherm and kinetics models are employed to understand the typical behavior of adsorbents/ethanol pairs.

4.2 Experiment for adsorption characteristics

4.2.1 Test rig for adsorption uptake measurement

This experimental setup is used for measuring adsorption uptake of ethanol onto the developed EG contained composite adsorbents. It comprises mainly an adsorber, an evaporator, two constant temperature water baths, and two water circulators as shown in Fig. 4.1. Adsorber is a small stainless steel cylinder of 40 mm diameter and 40 mm height whilst K-type thermocouple is inserted to measure adsorbent temperature. The evaporator

is a glass tube of 10 mm outer diameter, 1.6 mm wall thickness and 174 mm height where the K-type thermocouple is inserted to measure the evaporator temperature. Two constant temperature water baths of type TBN302DA along with two water circulators of type CTP3000 have been used to control the adsorber and evaporator temperatures. A rotary vacuum pump of type ULVAC (GCD-136X) has been used to evacuate the system. A Pirani gauge of type PG-D5A is used to test the vacuum condition of the system whilst AP10-32 type pressure transducer is used to measure the system pressure. A digital microscope of type NRM-D-2XZ with a minimum resolution of 0.01 mm has been used to measure the height of ethanol level in the evaporator before and after conducting adsorption process. The weight of adsorbent samples has been measured using Sartorius Practum 124-1S analytical lab balance with 120 grams weight capacity and readability of ± 0.1 mg. To avoid any condensation during the adsorption process, a tape heater surrounds the connecting tubes between evaporator and adsorber.

The experimental procedure can be summarized as follows:

- i) Prior to conducting adsorption uptake measurements, the composite adsorbent is dried using an oven for about 12 hours at 120°C. After that, the sample weight is measured.
- ii) The composite adsorbent is then placed into the adsorber and regenerated under vacuum condition for more than 3 hours at a temperature of 80°C.
- iii) The evaporator temperature is kept constant at 5°C whilst the adsorber temperature is maintained at 70°C. The height of ethanol onto the evaporator is then measured using the digital microscope. The valve between the evaporator and adsorber is opened where ethanol vapor flows to the adsorbent sample. After reaching the equilibrium condition, the ethanol height inside the evaporator is measured again to determine the amount of ethanol adsorbed.
- iv) The valve between the evaporator and adsorber is closed and the adsorber temperature is cold down to 60°C. The valve is then opened and adsorption process is carried out. The same procedure is repeated at adsorption temperatures of 50, 40, 30 and 20°C.
- v) To measure the isobaric adsorption corresponding to the evaporator temperature of 10°C and 15°C, steps (i) and (iv) have been repeated.

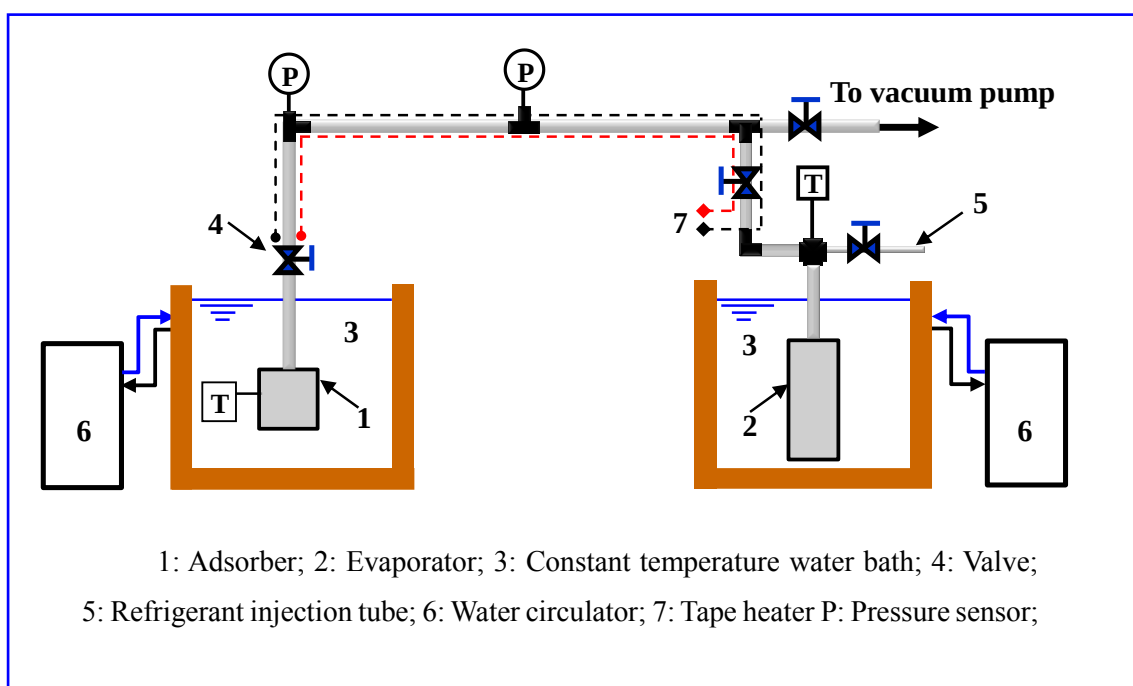


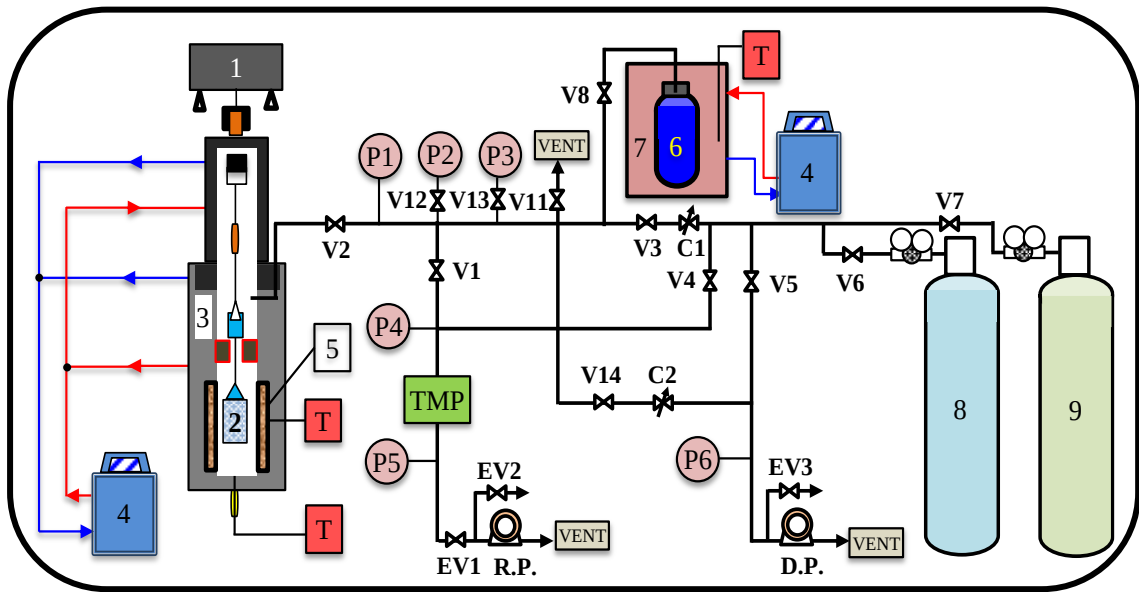
Fig. 4.1 Schematic diagram of the experimental apparatus for measuring adsorption uptake of ethanol onto composite adsorbents.

4.2.2 Gravimetrically adsorption uptake measurement

The gravimetric based magnetic suspension adsorption measurement unit (Rubotherm of type MSB-VG-S2), supplied by MicrotracBEL, Japan is employed for measurement of equilibrium uptake and kinetics of ethanol on rest of the studied adsorbents. Fig. 4.2 shows the schematic diagram of the magnetic suspension adsorption measurement unit. The major components of the experimental system are magnetic suspension balance unit; isothermal circulation oil baths to maintain adsorber and evaporator temperatures; isothermal air bath to avoid condensation through connecting tubes; a series of vacuum pumps including diaphragm, rotary, and turbo-molecular types. Weight measurement repeatability of magnetic balance is $\pm 30\mu\text{g}$ with a relative error of $\pm 0.002\%$ of the reading. The system employs nitrogen gas to operate the valves whilst pressurized helium gas is used for checking the leakage as well as to compute the void volume that is essential for buoyancy measurement. Three types of absolute pressure gauges (1) 3500 kPa, Keller PAA-35XHTT-35; (2) 133.3 kPa, MKS 628B13TBE1B; and (3) 1.33 kPa, MKS 628B12TBE1B are used in parallel to measure the ethanol vapor pressure with an accuracy of 0.15-0.25%F.S. The temperature of refrigerant has been

measured and maintained precisely by platinum resistance temperature element (100Ω) together with pressure instruments which assist in temperature tuning to the corresponding to ethanol vapor pressure [16,55,104].

The system executes the whole experiment automatically by following the instruction given in the software. It can be mentioned that buoyancy effect on the measurements is considered automatically by the system. Adsorption characteristics of ethanol onto prepared ACs have been investigated at five different temperatures namely 30, 40, 50, 60, and 70°C with various evaporator pressures. Experimental procedure can be described as follows; at first, the adsorbent is put into the adsorbent cell basket. The adsorbent is then regenerated at 120°C for 3 hours under vacuum condition for degassing the adsorbents. After regeneration, adsorbents are cooled to the specified adsorption temperature, and meanwhile, the ethanol (refrigerant) temperature is maintained at first set point of evaporation temperature. Once the temperatures on adsorbent and refrigerant side become steady, the valves are opened for adsorption automatically. The system records data for every second until the equilibrium condition is reached and then the refrigerant temperature is increased to next measuring point. Similarly, ethanol adsorption is recorded for all sets refrigerant temperatures. The same procedure has been adopted for every isotherm measurement.



1. Magnetic suspension balance; 2. Sample cell; 3. Circulation oil jacket; 4. Oil bath and circulator; 5. Sheathed heater; 6. Refrigerant container; 7. Isothermal oil bath; 8. Helium; 9. Nitrogen; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P6: Pressure gauges; C1-C2: Controlled valves; V1-V13: Valves.

Fig. 4.2 Schematic diagram of the experimental apparatus for measuring ethanol adsorption characteristics.

4.3 Theory of adsorption isotherm and kinetics models

4.3.1 Adsorption isotherms

Adsorption characteristic is crucial for designing AHP system. The behavior of equilibrium adsorption uptake of a particular pair entirely depends on adsorbent properties. Therefore, this section introduces popular adsorption isotherm models. Five well-known isotherm models namely Freundlich, Langmuir, Dubinin Astakhov (D-A), Dubinin Radushkevich (D-R), and Tóth equations have been employed to fit ethanol adsorption isotherms of all developed adsorbents as given by equations (4.1) to (4.5), respectively.

$$\frac{W}{W_0} = \left(\frac{P}{P_s} \right)^{1/k} \quad (4.1)$$

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT} P}}{1 + b_0 e^{\frac{Q_{st}}{RT} P}} \quad (4.2)$$

$$W = W_0 \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^n \right] \quad (4.3)$$

$$W = W_0 \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^2 \right] \quad (4.4)$$

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT}} P}{\left(1 + \left(b_0 e^{\frac{Q_{st}}{RT}} P \right)^h \right)^{1/h}} \quad (4.5)$$

A nonlinear method is used to optimize these model parameters to fit the experimental data for various pressures and temperatures. The root-mean-square deviation (RMSD) value between experimental and calculated adsorption uptake has been obtained according to the equation (4.6) for all studied isotherm models.

$$RMSD = \sqrt{\frac{\sum_{i=1}^N \left(\frac{W_{\text{experimental}} - W_{\text{calculated}}}{W_{\text{experimental}}} \times 100 \right)^2}{N}} \quad (4.6)$$

Where W is the equilibrium uptake [kg kg^{-1}], W_0 represents the maximum equilibrium uptake [kg kg^{-1}], P is the equilibrium pressure [kPa], P_s represents the saturation pressure [kPa], T denotes the adsorption temperature [K], R is the gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], Q_{st} is the isosteric heat of adsorption [kJ mol^{-1}], k and h are the dimensionless Freundlich and Tóth parameter respectively and n is the exponent of D-A equation.

4.3.2 Adsorption kinetics

Instantaneous adsorption uptake for particular adsorbent/adsorbate pair plays a significant role in designing and optimizing the performance of adsorption heat pump system. This section discusses the two classical adsorption kinetics models namely linear driving force (LDF) and Fickian diffusion (FD) for expressing the ethanol vapor adsorption kinetics of biomass-based activated carbons. Linear driving force (LDF) model is given by the equation (4.7) [16,104].

$$F = \frac{W(t) - W(\text{initial})}{W(\infty) - W(\text{initial})} = 1 - \exp \left(-F_o \frac{D_s t}{R_p^2} \right) \quad (4.7)$$

Where, $W(t)$ and $W(\infty)$ denote the instantaneous and equilibrium adsorption uptake in kg kg^{-1} , respectively. F_o represents the geometric parameter for adsorbent particle shape and

equal to 15 for spherical shape adsorbent particle. D_s and R_p are the surface diffusion coefficient [$\text{m}^2 \text{s}^{-1}$] and the radius of the adsorbent particle [m], respectively.

The linearized form of equation (4.7) can be written as:

$$\ln(1-F) = -F_o \frac{D_s t}{R_p^2} \quad (4.8)$$

Fickian diffusion (FD) model can be written as:

$$F = \frac{W(t) - W(\text{initial})}{W(\infty) - W(\text{initial})} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-F_o n^2 \pi^2 \frac{D_s t}{R_p^2}\right) \quad (4.9)$$

Equation (4.9) converges quickly in the long time region and higher terms of the summation become negligibly small; therefore, the equation (4.9) can be simplified into the equation (4.10) at longer times [16,104].

$$F = 1 - \frac{6}{\pi^2} \exp\left(-F_o n^2 \pi^2 \frac{D_s t}{R_p^2}\right) \quad (4.10)$$

The linearized form of equation (4.11) can be expressed as:

$$\ln(1-F) = \ln \frac{6}{\pi^2} - F_o n^2 \pi^2 \frac{D_s t}{R_p^2} \quad (4.11)$$

4.4 Biomass-derived AC/ethanol pairs

4.4.1 Adsorption isotherm

The detailed synthesis of biomass-derived ACs is discussed in chapter 3. Among series of AC samples for both biomasses (WPT and mangrove), the author has been selected optimized AC sample WC600A900K6 from WPT, named as WPT-AC, and MC600A900K6 from mangrove, named as M-AC, for adsorption isotherm and kinetics analysis. So, WPT-AC and M-AC named are used instead of WC600A900K6 MC600A900K6, respectively in this chapter. Fig. 4.3 describes equilibrium absorption amount of ethanol onto WPT-AC (WC600A900K6) whilst Fig. 4.4 represents adsorption amount for M-AC (MC600A900K6)/ethanol pair at temperatures 30 to 70°C with various pressures. For both adsorbent/adsorbate pairs, it is found that Freundlich, Langmuir model does not fit well with the experimental data. However, there is a good agreement between experimental and predicted adsorption uptake using D-A and Tóth equations within $\pm 10\%$ root-mean-square deviation (RMSD). In both figures, open triangle symbols represent the measured uptakes whereas lines denote the studied isotherm models. Isotherm parameters

of the studied models have been summarized in Table 4.2. It is important to mention that ethanol adsorption onto WPT-AC is as high as 1.90 kg kg^{-1} whereas one kg of M-AC adsorbs up to 1.65 kg of ethanol.

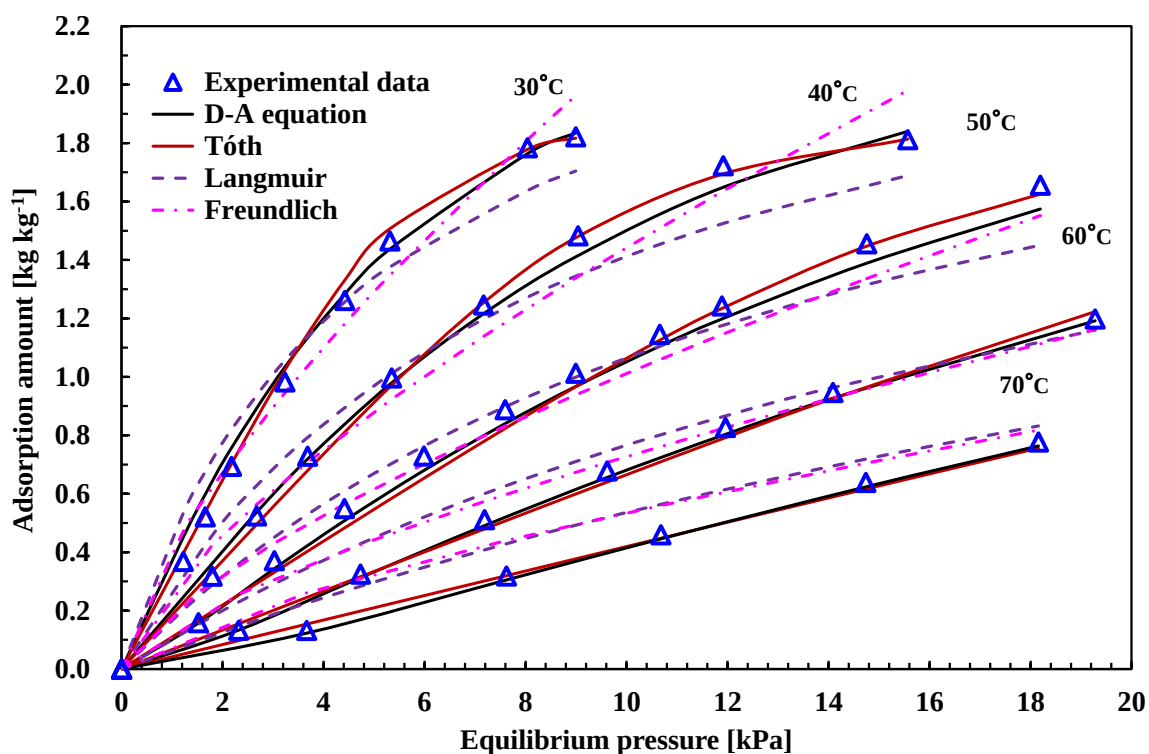


Fig. 4.3 Adsorption isotherms of ethanol onto WPT-AC (WC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, Tóth model).

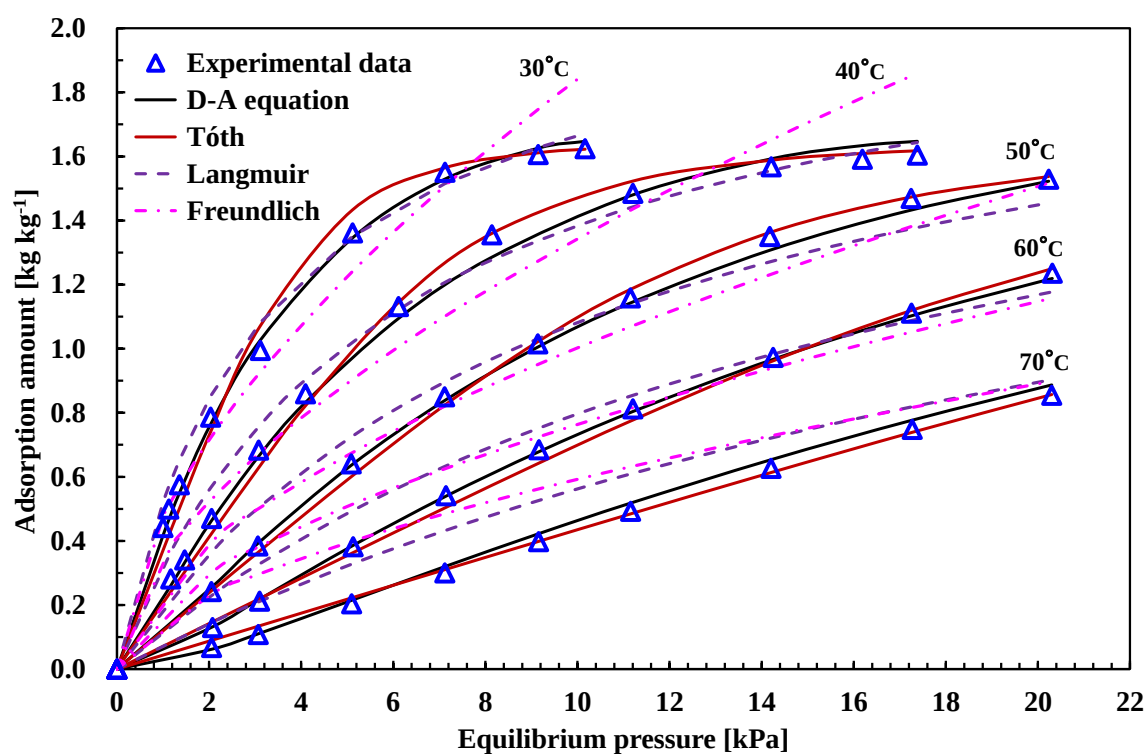


Fig. 4.4 Adsorption isotherms of ethanol onto M-AC (MC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, Tóth model).

Table 4.2 Fitting parameters of the studied isotherm models for ethanol adsorption onto WPT-AC and M-AC adsorbents.

Model	Fitting parameters	WPT-AC (WC600A900K6)	M-AC (MC600A900K6)
Freundlich	W_0 [kg kg ⁻¹]	2.2	1.9
	k [-]	1.4	1.7
	RMSD [%]	25.8	52
D-A	W_0 [kg kg ⁻¹]	1.9	1.65
	E [kJ kg ⁻¹]	91.55	105.91
	n [-]	1.43	1.62
	RMSD [%]	5.43	3.40
Langmuir	W_0 [kg kg ⁻¹]	2.6	2.2
	Q_{st} [kJ mol ⁻¹]	45.4	47.66
	b_0 [kPa ⁻¹]	3.18×10^{-9}	1.91×10^{-9}
	RMSD [%]	19.6	30
Tóth	W_0 [kg kg ⁻¹]	1.9	1.65
	Q_{st} [kJ mol ⁻¹]	44.23	46.30
	h [-]	3.88	3.42
	b_0 [kPa ⁻¹]	4.09×10^{-9}	2.37×10^{-9}
	RMSD [%]	5.13	8.24

4.4.2 Adsorption kinetics

Fig. 4.5 and Fig. 4.6 show the temporal histories of adsorption uptake and pressure of WPT-AC/ethanol pair at adsorption temperature 40°C and 70°C respectively. It can be seen that at each adsorption step uptake increased continuously until equilibrium condition corresponds to evaporation pressure. Fig. 4.7 and Fig. 4.8 describe the similar plot of adsorption uptake and evaporation pressure versus time at an adsorption temperature of 40

and 70°C for M-AC/ethanol pair, respectively. Similar trends are also observed for M-AC/ethanol adsorption. Two classical adsorption kinetics models namely Linear driving force (LDF) and Fickian diffusion (FD) have been employed to express the ethanol vapor adsorption kinetics of biomass-based activated carbons.

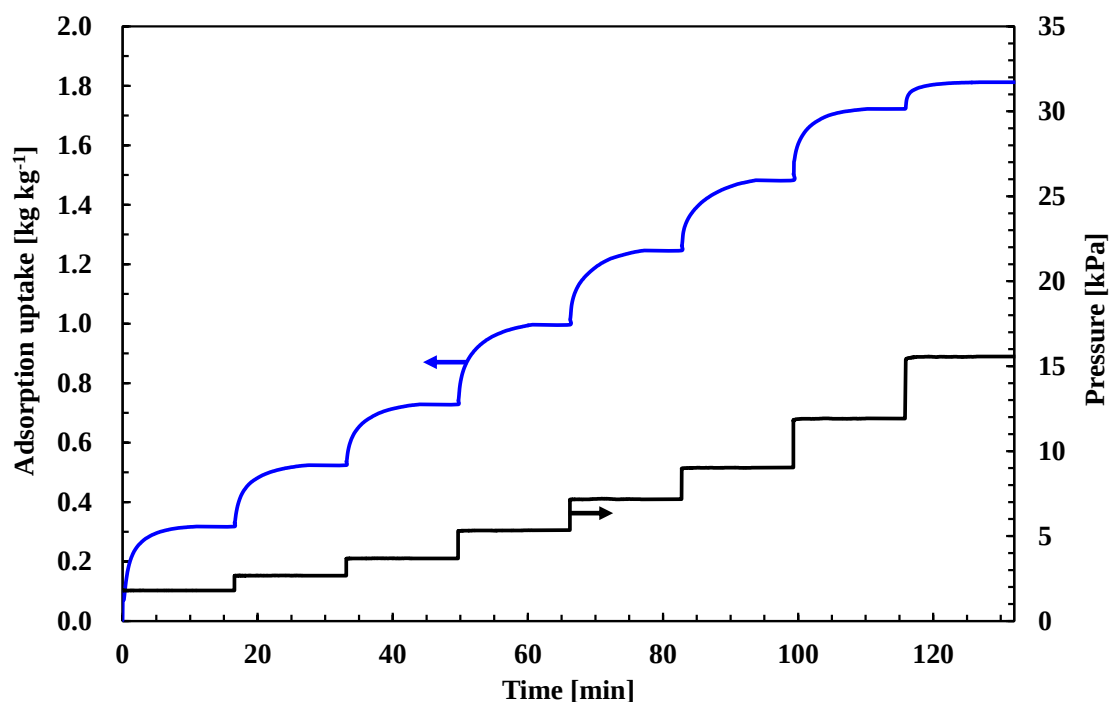


Fig. 4.5 Temporal histories of adsorption uptake and pressure of WPT-AC/ethanol pair at adsorption temperature 40°C.

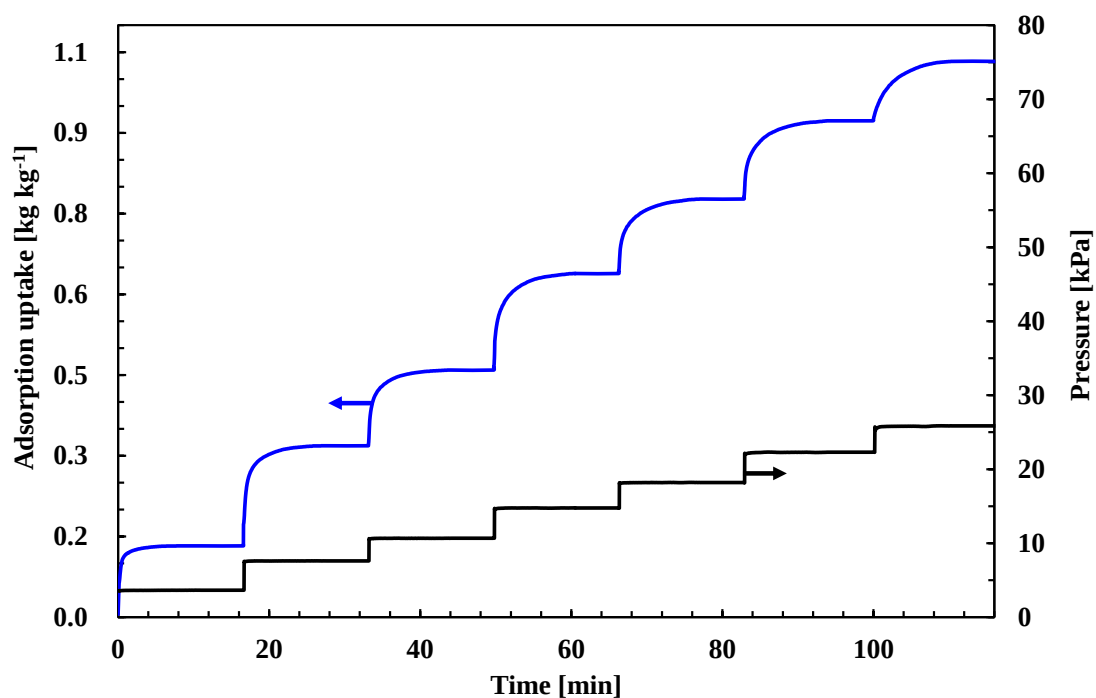


Fig. 4.6 Temporal histories of adsorption uptake and pressure of WPT-AC/ethanol pair at adsorption temperature 70°C.

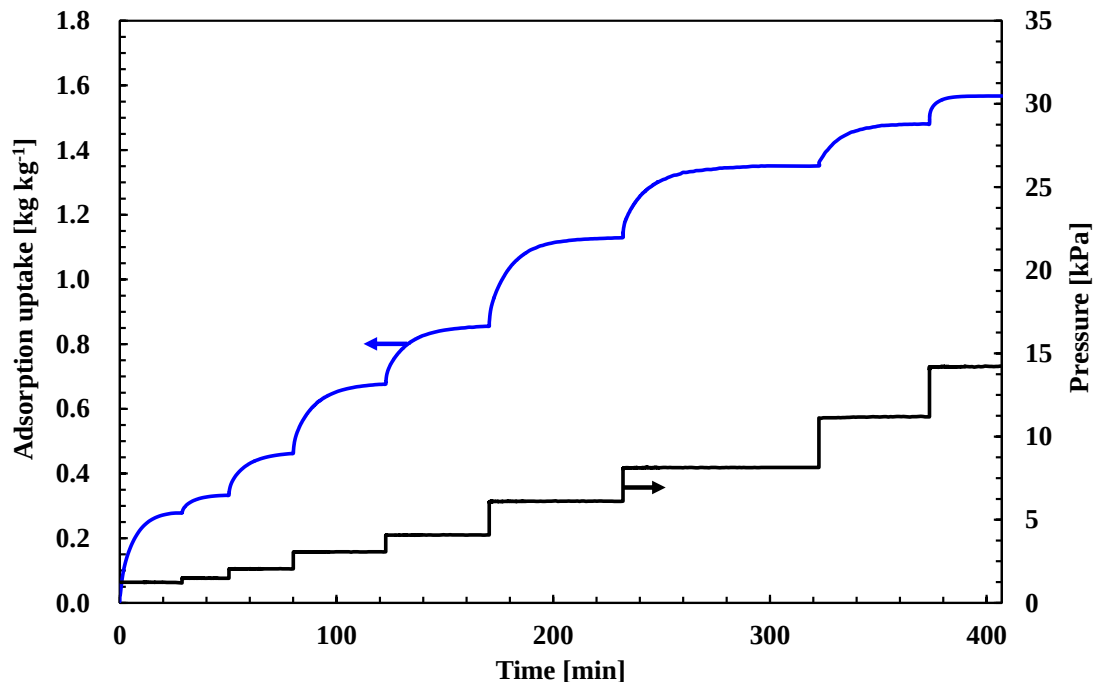


Fig. 4.7 Temporal histories of adsorption uptake and pressure of M-AC/ethanol pair at adsorption temperature 40°C.

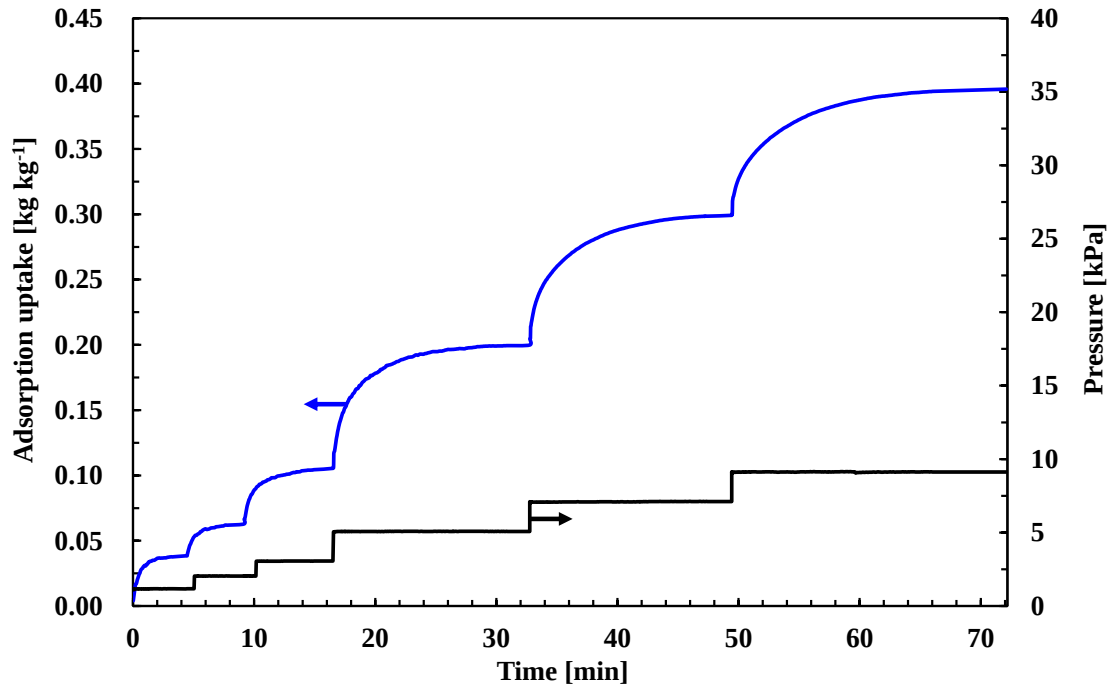


Fig. 4.8 Temporal histories of adsorption uptake and pressure of M-AC/ethanol pair at adsorption temperature 70°C.

Fig. 4.9 shows the plot of $\ln(1 - F)$ versus time for WPT-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 2.18 kPa. Similarly, the plot of $\ln(1 - F)$ versus time for M-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 5.12 kPa is shown in Fig. 4.10. From both pairs, it is observed that LDF model represents better agreement than FD model. Fig. 4.11 and Fig. 4.12 describe the fractional uptake versus time for WPT-AC/ethanol pair and M-AC/ethanol pair, respectively, at an adsorption temperature of 30, 50 and 70°C. Diffusion time constant (D_s/R_p^2) at each evaporator pressure step for WPT-AC/ethanol and M-AC/ethanol pairs has been presented in Table 4.3. It is observed that adsorption rate of WPT-AC/ethanol pair is higher than M-AC/ethanol pair.

Surface diffusion describes the mass transfer behavior, therefore, the classical Arrhenius equation, which is shown in the equation (4.12), is employed to illustrate surface diffusion, activation energy, adsorption temperature and adsorbent radius.

$$D_s = D_{so} \exp\left(\frac{E_a}{RT}\right) \quad (4.12)$$

Dividing on both side of the equation (4.12) by R_p^2 and linearization form of this equation can be written as:

$$\ln\left(\frac{D_s}{R_p^2}\right) = \ln\left(\frac{D_{so}}{R_p^2}\right) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (4.13)$$

Where, E_a and D_{so} denote the activation energy in kJ kg^{-1} and pre-exponential constant in $\text{m}^2 \text{s}^{-1}$, respectively. At each adsorption temperature, the average values of diffusion time constant have been calculated for both pairs. Fig. 4.13 shows the plot of $\ln(D_s/R_p^2)$ versus the inverse of adsorption temperature ($1/T$) for both samples. From the figure, it can be observed that for both pairs that relationship (D_s/R_p^2) versus the inverse adsorption temperature ($1/T$) complies with the classical Arrhenius equation. The numerical values of E_a and D_{so}/R_p^2 have been estimated from the slope and intercept of the linear plot (D_s/R_p^2) versus the inverse adsorption temperature ($1/T$). Numerical values of both pairs are presented in Table 4.4. It can be mentioned that WPT-AC/ethanol pair shows the activation energy $309.62 \text{ kJ kg}^{-1}$ whilst $467.30 \text{ kJ kg}^{-1}$ is for M-AC/ethanol pair.

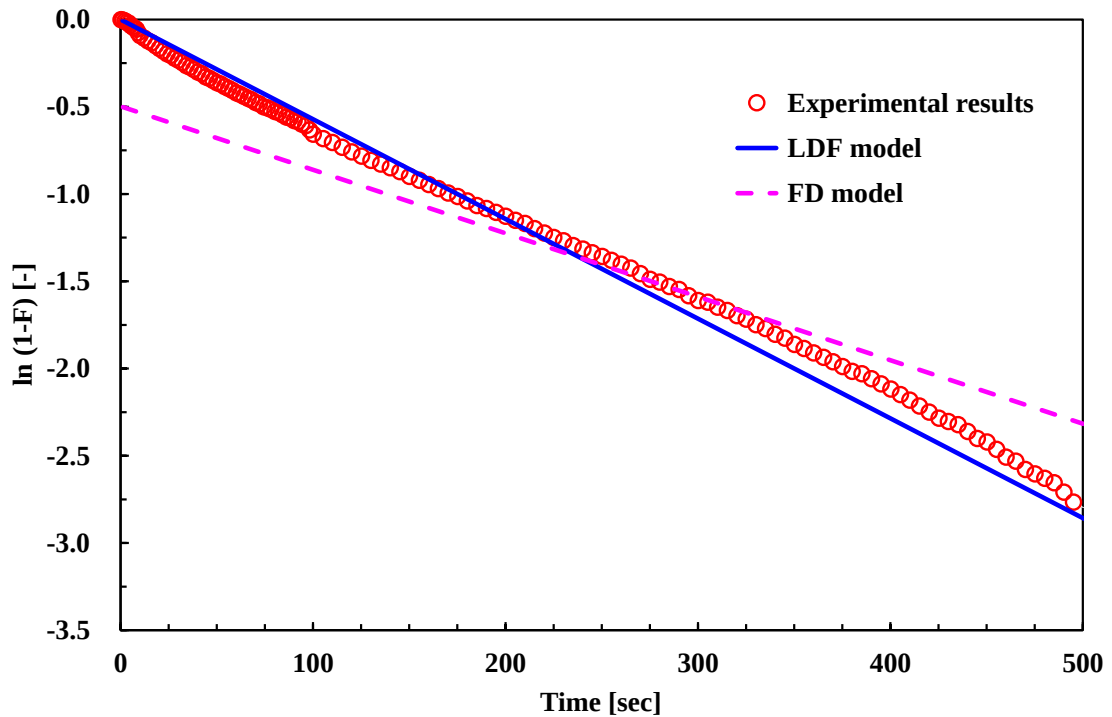


Fig. 4.9 Plot of $\ln(1 - F)$ versus time for WPT-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 2.18 kPa .

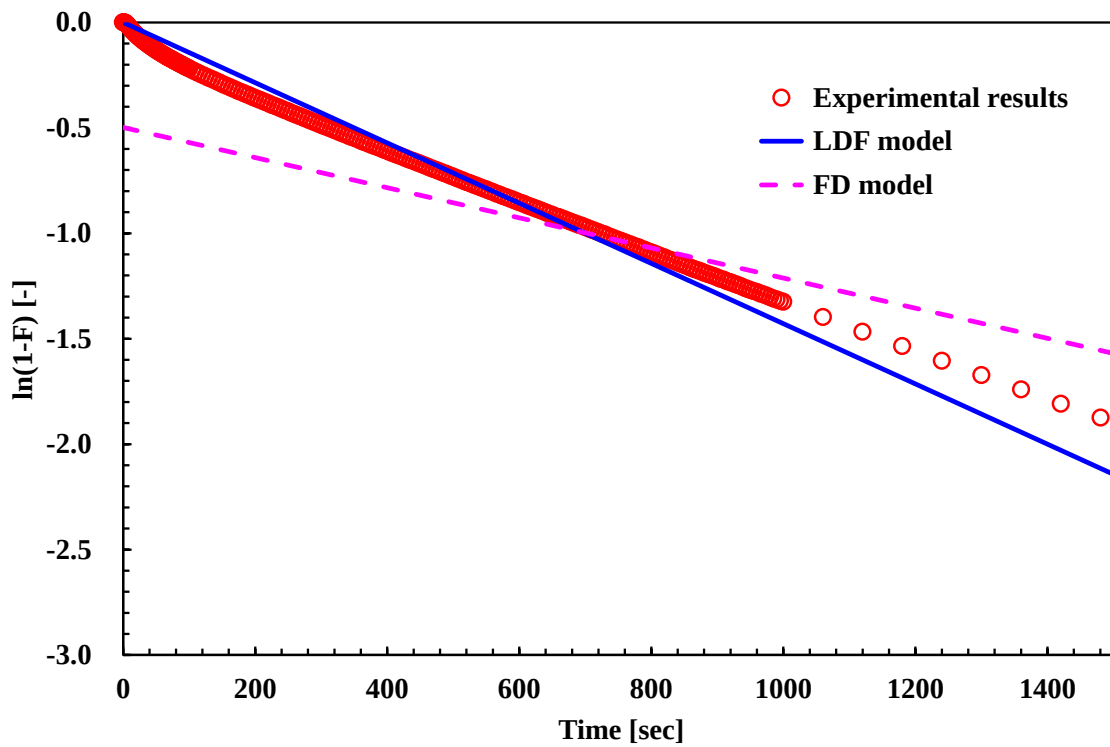


Fig. 4.10 Plot of $\ln(1 - F)$ versus time for M-AC/ethanol pair at 30°C adsorption temperature and evaporator pressure of 5.12 kPa.

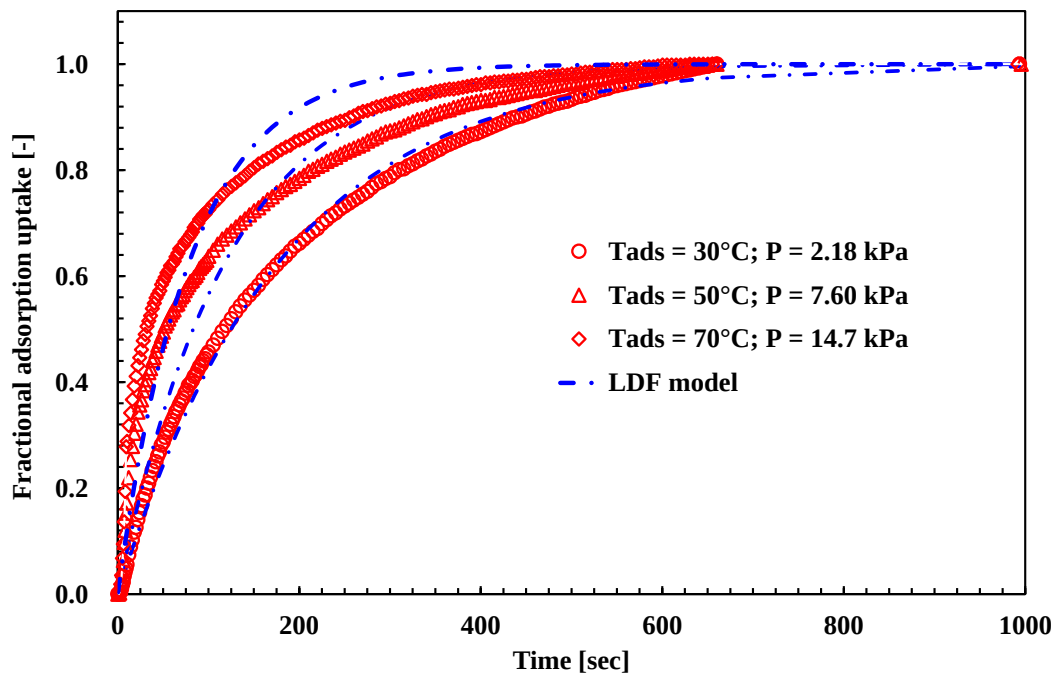


Fig. 4.11 Fractional uptake versus time for WPT-AC/ethanol pair at adsorption temperature 30, 50 and 70°C (symbols represent experiments and dash dot lines represent LDF model).

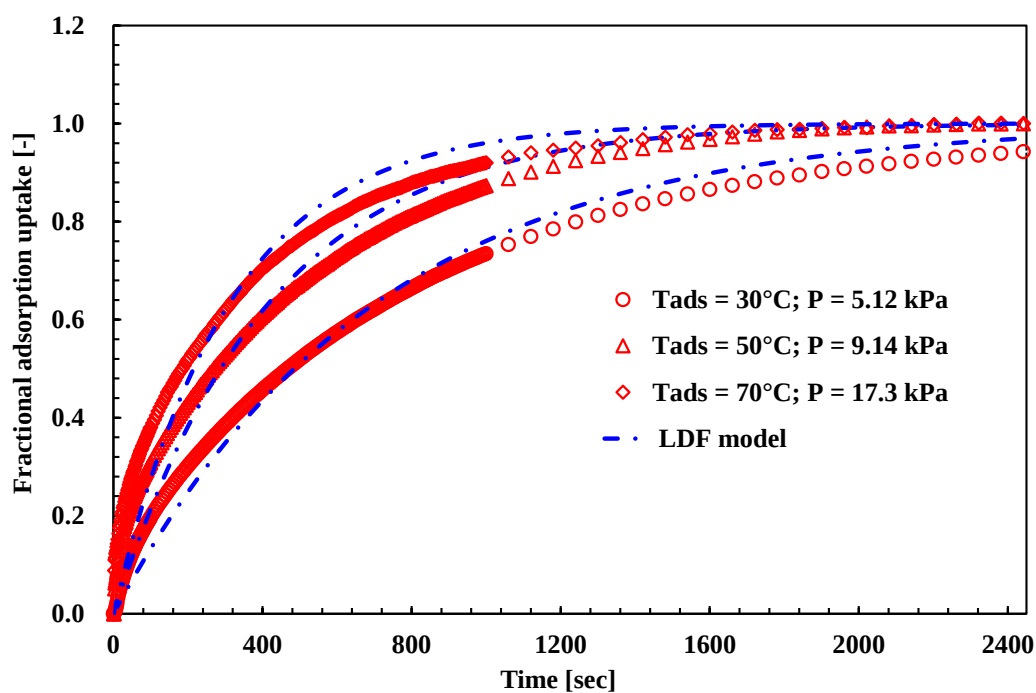


Fig. 4.12 Fractional uptake versus time for M-AC/ethanol pair at adsorption temperature 30, 50 and 70°C (symbols represent experiments and dash dot lines represent LDF model).

Table 4.3 Adsorption kinetics parameters of WPT-AC/ethanol and M-AC/ethanol pairs.

Adsorption kinetics parameters of WPT-AC/ethanol pair			Adsorption kinetics parameters of M-AC/ethanol pair		
T_{ads} [°C]	P [kPa]	D_s/R_p^2 [s ⁻¹]	T_{ads} [°C]	P [kPa]	D_s/R_p^2 [s ⁻¹]
30.08	1.66	4.04E-04	30	2.03	9.52E-05
30.01	2.18	3.70E-04	29.99	3.11	9.80E-05
30.01	3.23	3.81E-04	30.03	5.12	9.01E-05
30.02	4.42	3.70E-04	29.95	7.12	8.89E-05
30	5.31	3.60E-04			
40.14	2.67	5.33E-04	40.01	2.05	1.59E-04
40	3.68	4.94E-04	40	3.08	1.29E-04
40	5.35	4.94E-04	40	4.10	1.39E-04
40	7.17	4.94E-04	39.97	6.12	1.39E-04
39.98	9.04	4.83E-04			
49.98	7.60	5.56E-04	50	5.09	1.59E-04
49.98	9.00	5.56E-04	50	7.11	1.71E-04
50	10.66	5.33E-04	50	9.14	1.61E-04
49.99	11.89	5.13E-04	49.97	11.15	1.55E-04
50	14.76	5.56E-04	50.01	14.17	1.53E-04
49.99	18.19	5.80E-04	49.99	17.25	1.85E-04
59.85	4.73	7.84E-04	60	7.15	2.30E-04
59.99	7.19	7.41E-04	60	9.17	2.07E-04
59.99	9.62	6.67E-04	60.02	11.20	1.83E-04
60.02	14.09	6.35E-04	60	14.25	1.80E-04
60.02	19.28	6.35E-04	60	17.26	1.67E-04
69.85	7.62	7.84E-04	70.07	7.12	3.70E-04
70	10.68	7.41E-04	70.06	9.16	3.25E-04
70	14.7	7.41E-04	70.02	11.15	2.72E-04
69.96	18.16	6.67E-04	69.94	14.21	2.56E-04
			69.97	17.27	2.15E-04

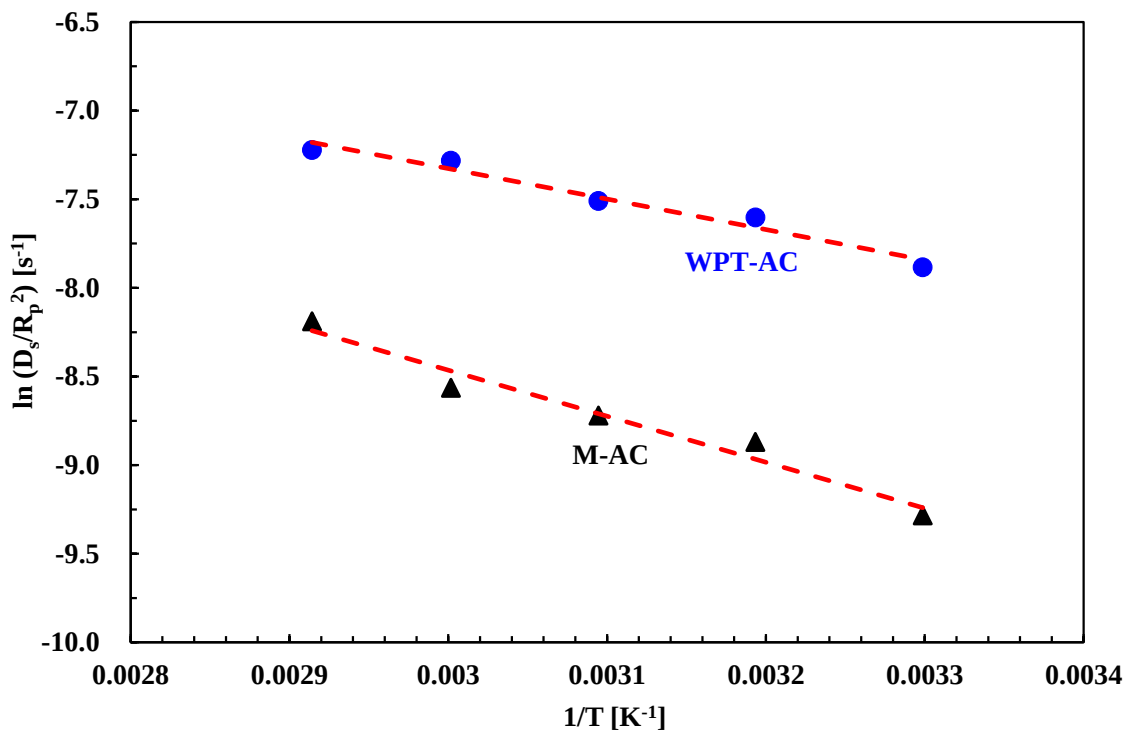


Fig. 4.13 Arrhenius plot of the WPT-AC/ethanol and M-AC/ethanol pairs.

Table 4.4 Parameters of Arrhenius equation for studied pairs.

Adsorbent/refrigerant pair	D_{so}/R_p^2 [s ⁻¹]	E_a [kJ kg ⁻¹]
WPT-AC/ethanol	1.15E-01	309.62
M-AC/ethanol	5.09E-01	467.30

Fig. 4.14 compares the net uptake for adsorption cooling cycle employing WPT-AC/ethanol (solid line) and M-AC/ethanol (dashed line) pairs. The evaporator, adsorption and desorption temperatures chosen are 7, 30 and 80°C, respectively. It can be seen that there is the only marginal difference in the net uptake for both the pairs, indicating that they should provide similar cooling throughput for an adsorption chiller. Fig. 4.15 represents the comparison between net uptake obtained for M-AC/ethanol (dashed line) and commercially available activated carbon namely, Maxsorb III/ethanol [16] (solid line) pairs at the above mentioned operating conditions. It is evident that M-AC/ethanol pair shows 35% higher net uptake than that of Maxsorb III/ethanol, making it a promising candidate for adsorption chiller.

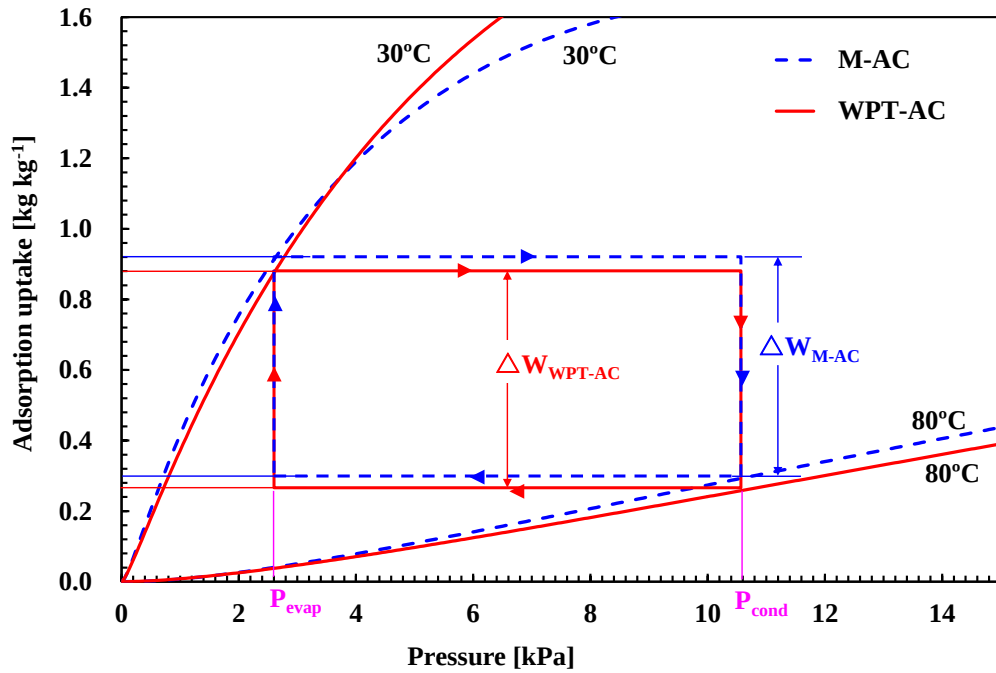


Fig. 4.14 Comparison between adsorption uptake difference of adsorption cooling cycles using WPT-AC/ethanol (solid line) and M-AC/ethanol (dashed line) pairs at evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively.

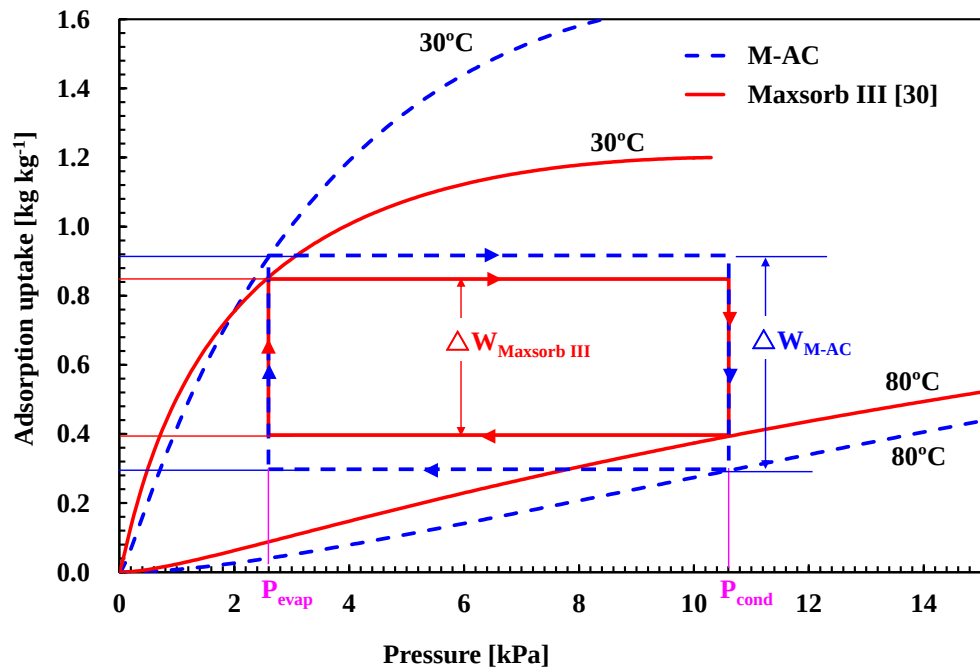


Fig. 4.15 Comparison between adsorption uptake difference of adsorption cooling cycles using M-AC/ethanol (dashed line) and Maxsorb III/ethanol (solid line) [16] pairs at evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively.

4.5 Composites/ethanol pairs

4.5.1 EG contained composites/ethanol pairs

4.5.1.1 Adsorption isotherms

In chapter 3 discussed the properties of synthesized expanded graphite (EG) contained composites. Among them, composite A and composite C have been chosen for ethanol adsorption characteristics. The Dubinin Radushkevich (D-R) and Dubinin Astakhov (D-A) equations have been used, respectively, to fit adsorption isotherms of composite A (50% Maxsorb III, 40% EG, 10% binder) and composite C (70% Maxsorb III, 20% EG, 10% binder). Numerical values of W_0 , E , and n for composite A/ethanol and composite C/ethanol pairs have been furnished in Table 4.5. Fig. 4.16 shows adsorption isobars of ethanol onto composite A at evaporation temperatures of 5, 10 and 15°C, the fitting of D-R equation is also superimposed on the same figure. The plot of adsorption uptake versus adsorption temperatures at the same evaporation temperatures for composite C/ethanol pair is also shown in Fig. 4.17. Adsorption equilibrium uptake predicted by D-A equation of composite C/ethanol pair is also presented in the same figure. It can be seen from Fig. 4.16 and Fig. 4.17 that there is a good agreement between experimentally measured adsorption equilibrium data and those predicted using D-R and D-A equations. It is also worth mentioning that the maximum adsorption uptake of composite A (50% Maxsorb III, 40% EG, 10% binder) and composite C (70% Maxsorb III, 20% EG, 10% binder) are, respectively, 0.61 and 0.89 kg kg⁻¹ which about 50% and 74% of maximum adsorption uptake of Maxsorb III/ethanol pair [8]. This is clear evidence that the binder does not sacrifice the adsorption capacity of Maxsorb III of the consolidated composites. Fig. 4.18 and Fig. 4.19 show the volumetric adsorption isotherms of composite A/ethanol and composite C/ethanol pairs. The volumetric uptake is estimated using the packing density of each composite. It can be seen from Fig. 4.18 and Fig. 4.19 that, composite A has the ability to adsorb about 325 kg m⁻³ of ethanol at an adsorption temperature of 30°C whilst composite C can adsorb ethanol as high as 380 kg m⁻³ at the same adsorption temperature. Fig. 4.20 shows the comparison between volumetric uptake difference of adsorption cooling cycles employing composite C/ethanol (solid line ABCD) and Maxsorb III/ethanol (dashed line abcd) pairs at the evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively. The packing density of Maxsorb III powder has been measured using Micromeritics: GeoPyc 1360 Pycnometer provided by

Micromeritics Instrument Corporation and found to be 290 kg m^{-3} . It can be seen from Fig. 4.20 that, volumetric uptake difference of composite C/ethanol pair is about 21% higher than that of Maxsorb III/ethanol.

Table 4.5 Isotherm parameters of ethanol adsorption onto of the studied composites.

Composite	$W_0 [\text{kg kg}^{-1}]$	$E [\text{kJ kg}^{-1}]$	$n [-]$
A: 50% Maxsorb III, 40% EG, 10% binder	0.61	125	2
C: 70% Maxsorb III, 20% EG, 10% binder	0.89	119	1.8

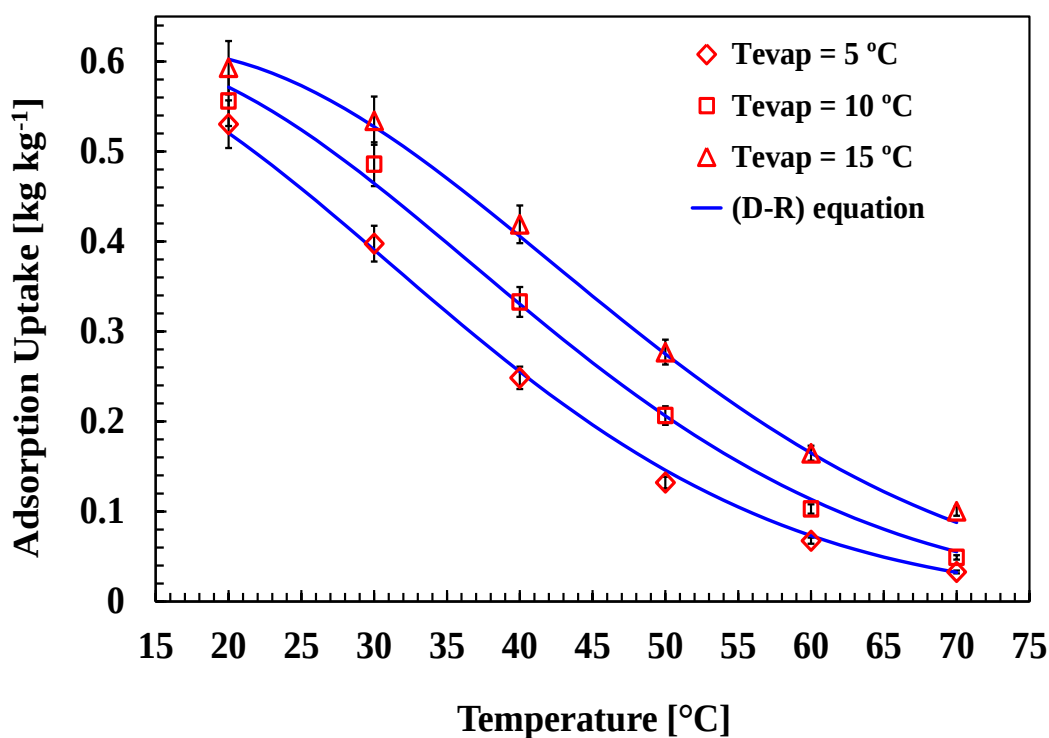


Fig. 4.16 Adsorption isobars of ethanol onto composite A (50% Maxsorb III, 40% EG, 10% binder) with packing density of 517 kg m^{-3} (error bars of uptake is $\pm 5\%$).

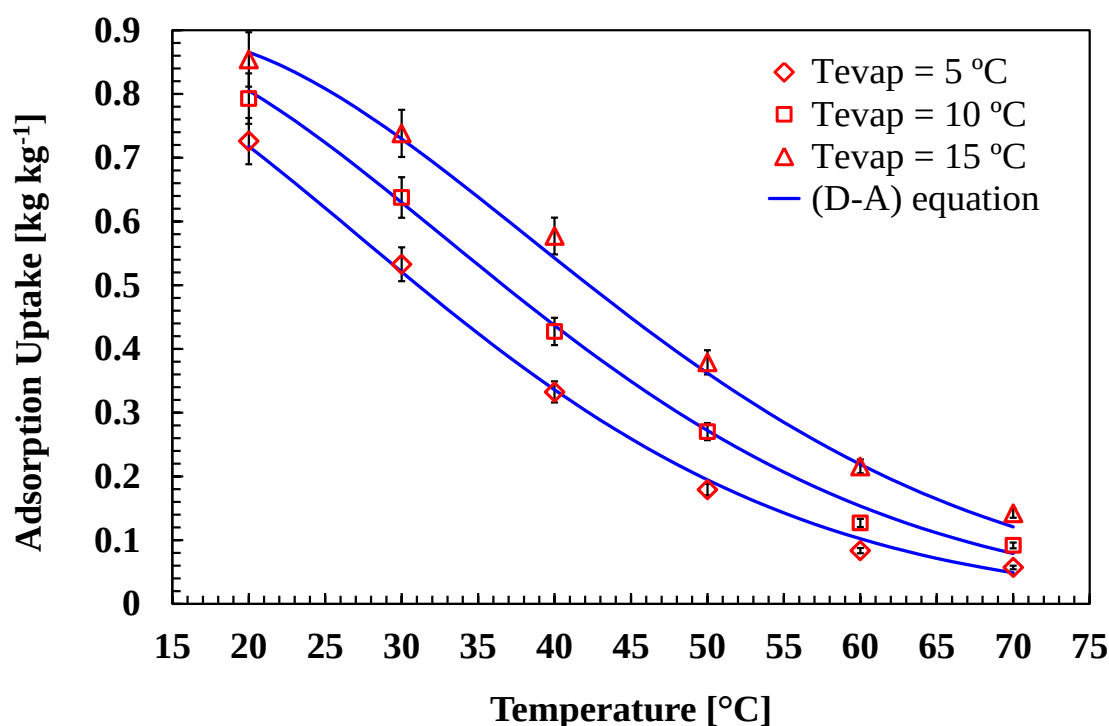


Fig. 4.17 Adsorption isobars of ethanol onto composite C (70% Maxsorb III, 20% EG, 10% binder) with packing density of 446 kg m^{-3} (error bars of uptake is $\pm 5\%$).

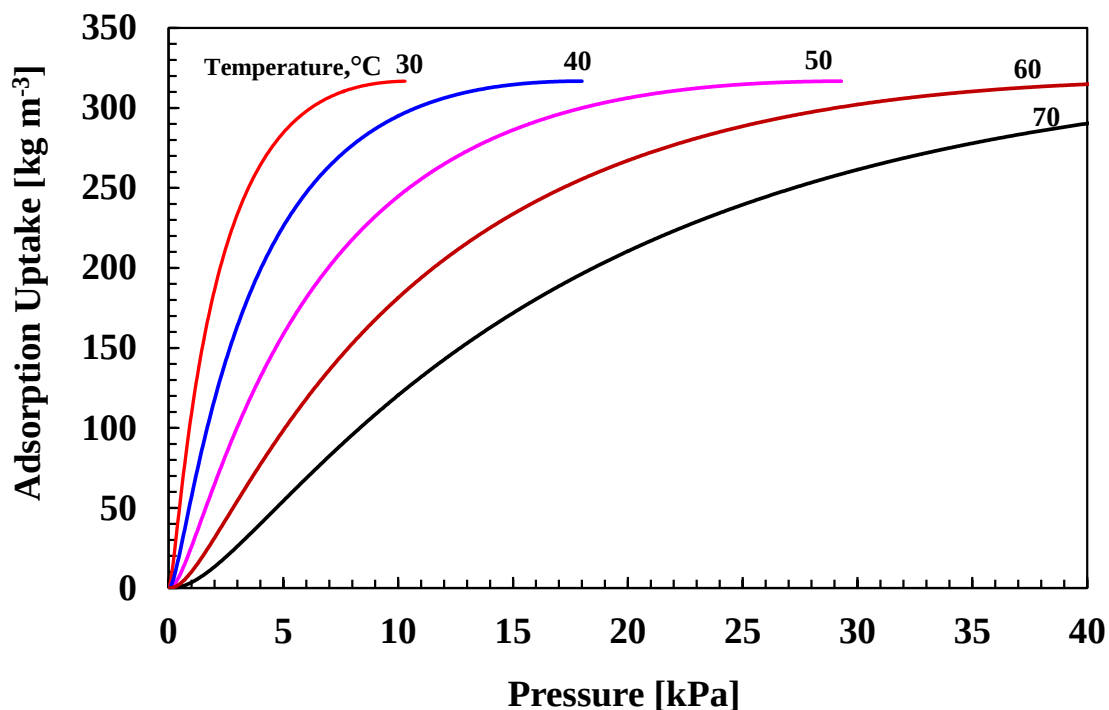


Fig. 4.18 Predicted volumetric adsorption isotherms of composite adsorbent A (50% Maxsorb III, 40% EG, 10% binder)/ethanol pair with packing density of 517 kg m^{-3} .

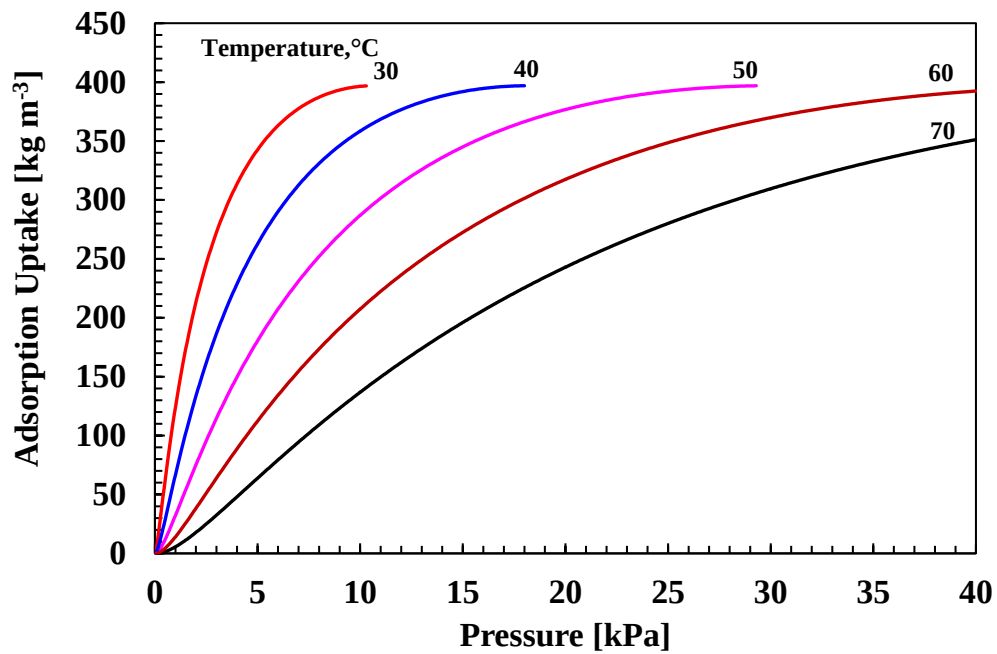


Fig. 4.19 Predicted volumetric adsorption isotherms of composite adsorbent C (70% Maxsorb III, 20% EG, 10% binder)/ethanol pair with packing density of 446 kg m^{-3} .

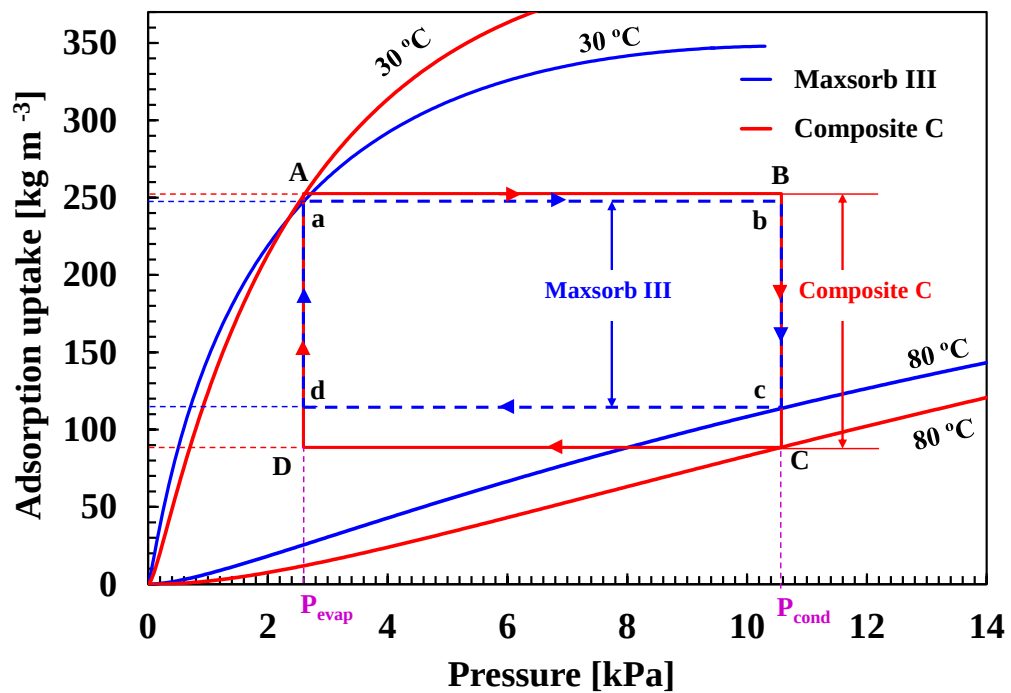


Fig. 4.20 Comparison between volumetric adsorption uptake difference of adsorption cooling cycles using Maxsorb III/ethanol and composite C/ethanol pairs at the evaporator, adsorption and desorption temperatures of 7, 30 and 80°C , respectively.

4.5.2 GNPs contained composites/ethanol pairs

4.5.2.1 Adsorption isotherms

Porous properties and thermal conductivity of synthesized graphene nanoplatelets (GNPs) and without GNPs contained carbon based composite were presented in chapter 3. This chapter presents the ethanol adsorption characteristics onto those developed composites. Plots of fitted Tóth and D-A equations are shown in Figs. 4.21 – 4.24 for composite 1, composite 2, composite 3, and composite 4, respectively. It is worthy to mention that there is a very good agreement between experimental and predicted adsorption uptake using D-A and Tóth equations within $\pm 5\%$ RMSD. In Figs. 4.21 – 4.24, open circle symbols represent the measured uptake whilst solid lines and dotted lines denote the D-A and Tóth equation, respectively. Optimized numerical values of studied isotherms model parameters are furnished in Table 4.6. It is observed that equilibrium ethanol adsorption amount is higher for composite 1 followed by composite 4, 2, and 3. This due to the higher BET surface area and pore volume of, which is also explained in chapter 3 in case of N_2 adsorption.

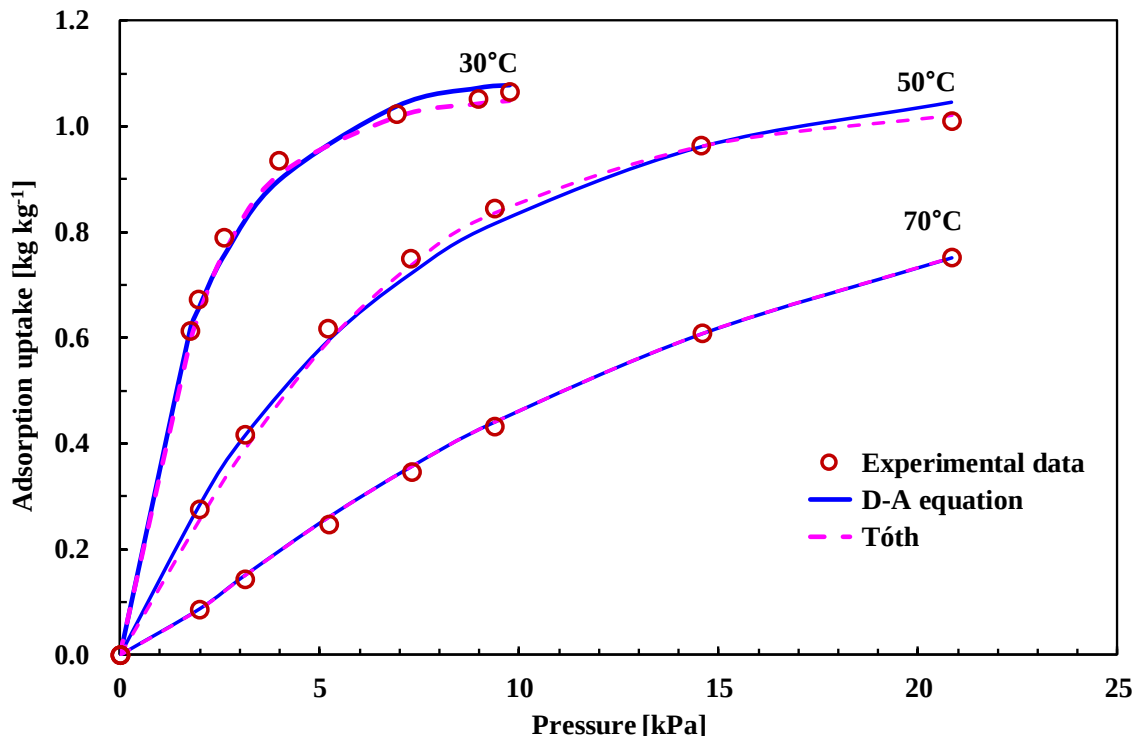


Fig. 4.21 Experimental data of composite 1 ($\rho = 316 \text{ kg m}^{-3}$) fitted with studied isotherm models.

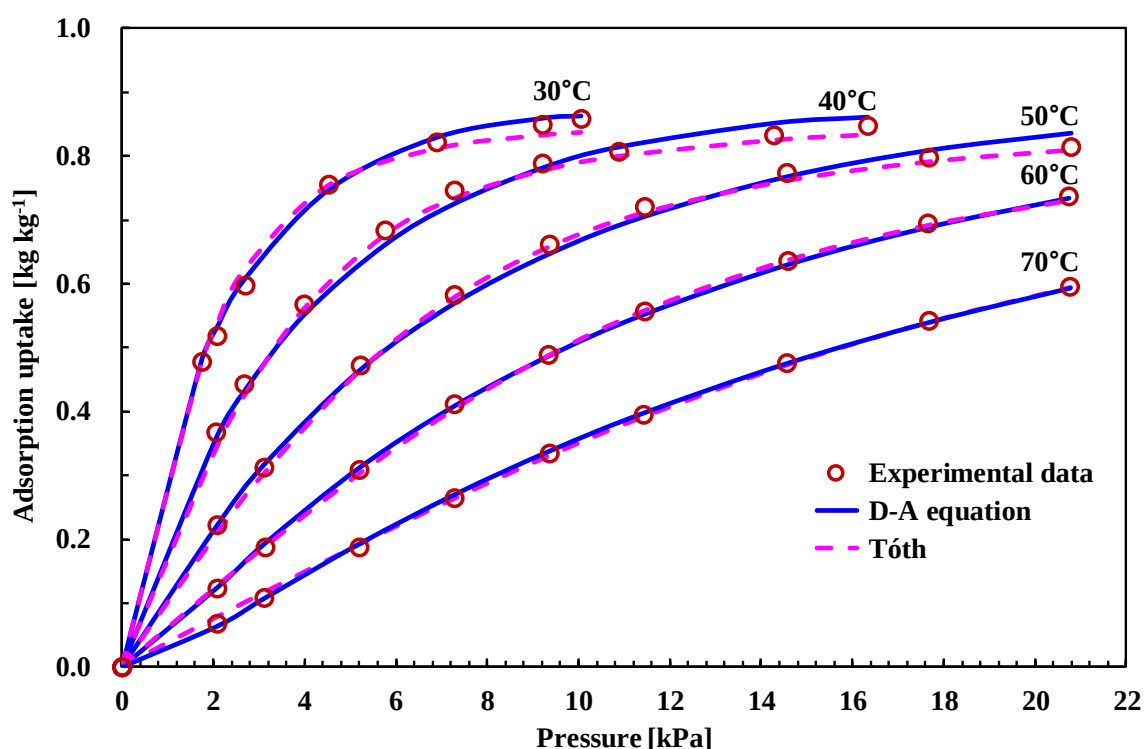


Fig. 4.22 Experimental data of composite 2 ($\rho = 399 \text{ kg m}^{-3}$) fitted with studied isotherm models.

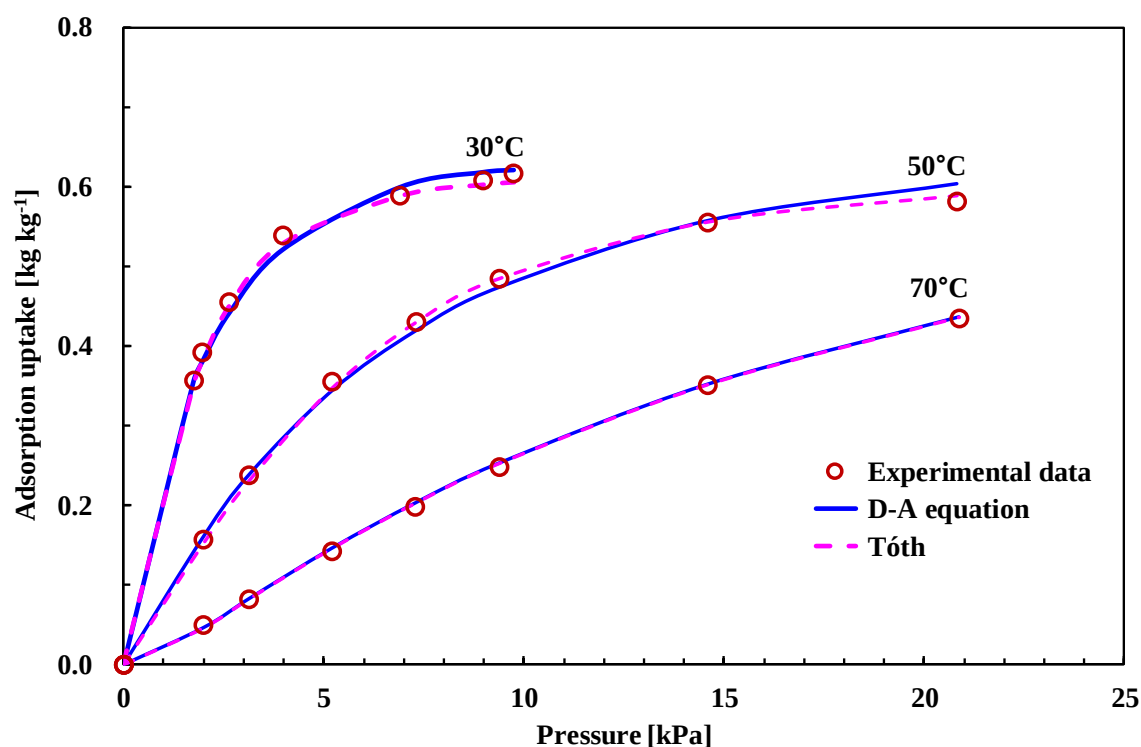


Fig. 4.23 Experimental data of composite 3 ($\rho = 498 \text{ kg m}^{-3}$) fitted with studied isotherm models.

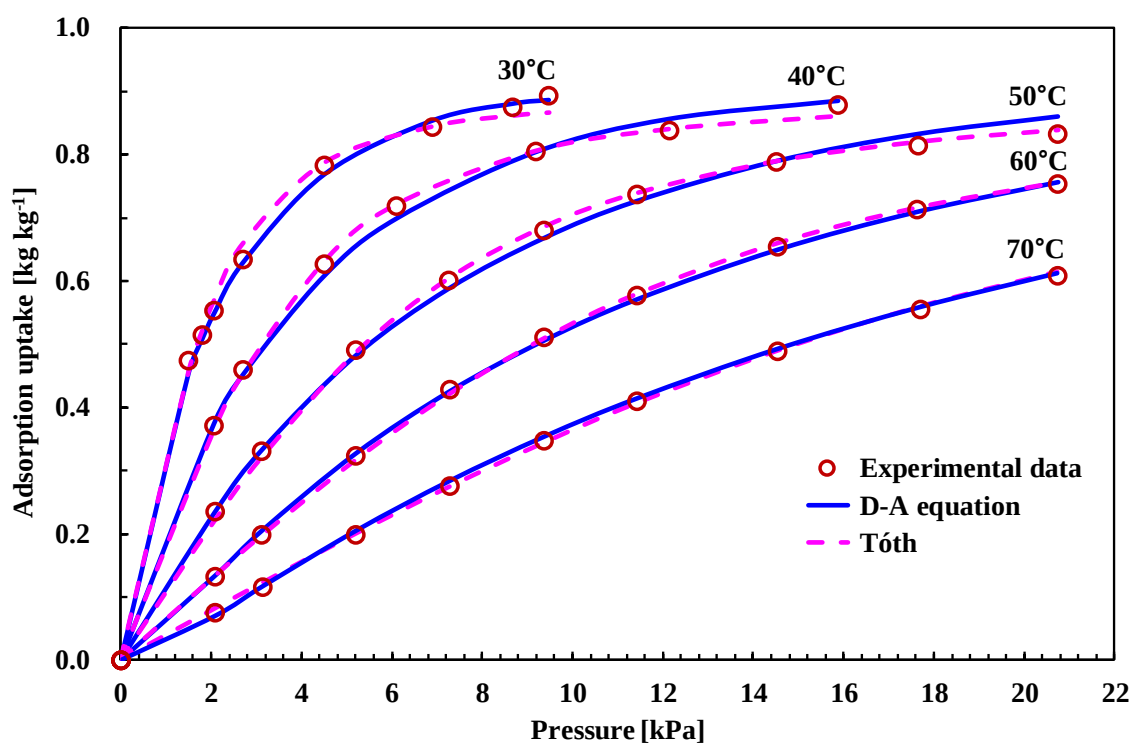


Fig. 4.24 Experimental data of composite 4 ($\rho = 388 \text{ kg m}^{-3}$) fitted with studied isotherm models.

Table 4.6 Fitting parameters of the studied isotherm models for studied composites/ethanol pairs.

Model	Fitting parameters	composite 1	Composite 2	Composite 3	Composite 4	Maxsorb III (parent adsorbent) [16]
D-A	W_0 [kg kg ⁻¹]	1.08	0.86	0.62	0.89	1.20
	E [kJ kg ⁻¹]	134.42	131.28	134.07	132.48	139.5
	n [-]	1.83	1.86	1.88	1.84	1.8
	RMSD [%]	2.932	1.841	2.480	1.834	-
Tóth	W_0 [kg kg ⁻¹]	1.08	0.86	0.62	0.89	
	Q_{st} [kJ mol ⁻¹]	44.99	46.02	45.12	46.99	
	t [-]	2.18	2.19	2.11	2.15	-
	b_0 [kPa ⁻¹]	6.50×10^{-9}	4.32×10^{-9}	6.40×10^{-9}	3.09×10^{-9}	
	RMSD [%]	4.489	3.329	1.939	2.274	

Fig. 4.25 shows the improvement of effective volumetric uptake of studied composites compare with Maxsorb III/ethanol pair at the evaporator, adsorption and desorption temperatures of 7, 30 and 80°C, respectively. The packing density of activated carbon (Maxsorb III) can be reached to 290 kg m⁻³ [46]. It is observed that all studied composites show higher effective volumetric uptake compare to Maxsorb III. Highest improvement is observed for composite 2, which is about 23% (Fig. 4.25). It is due to the compactness of composite material compare to the parent material.

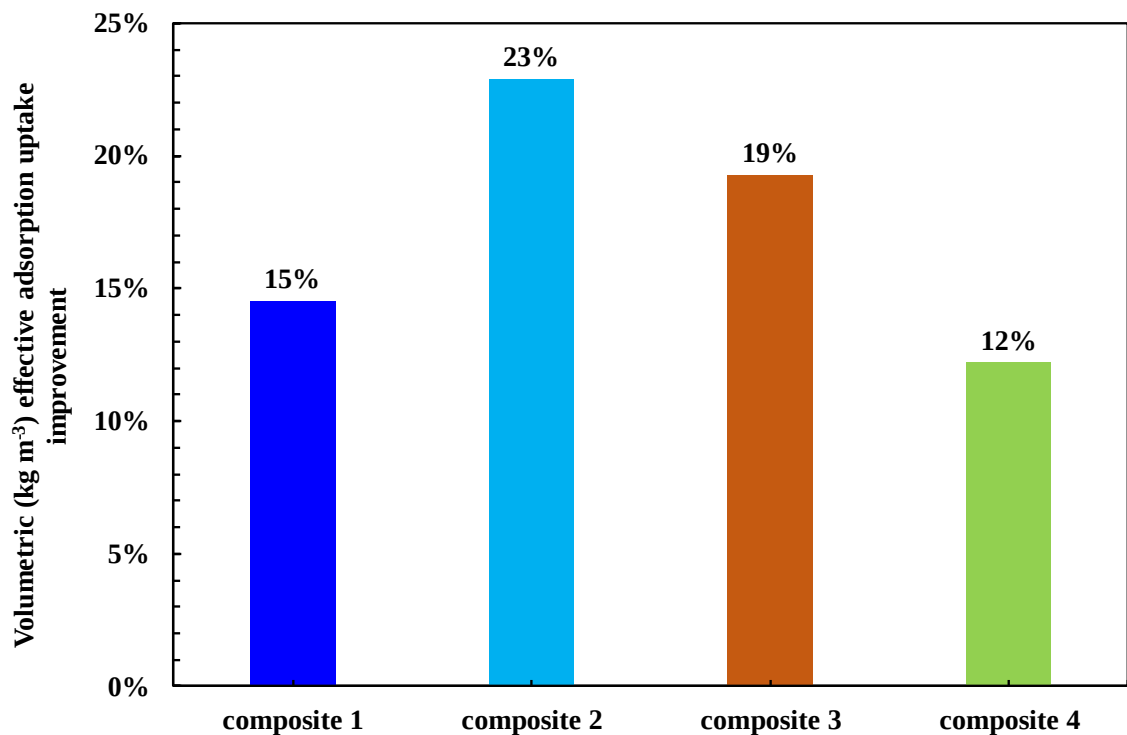
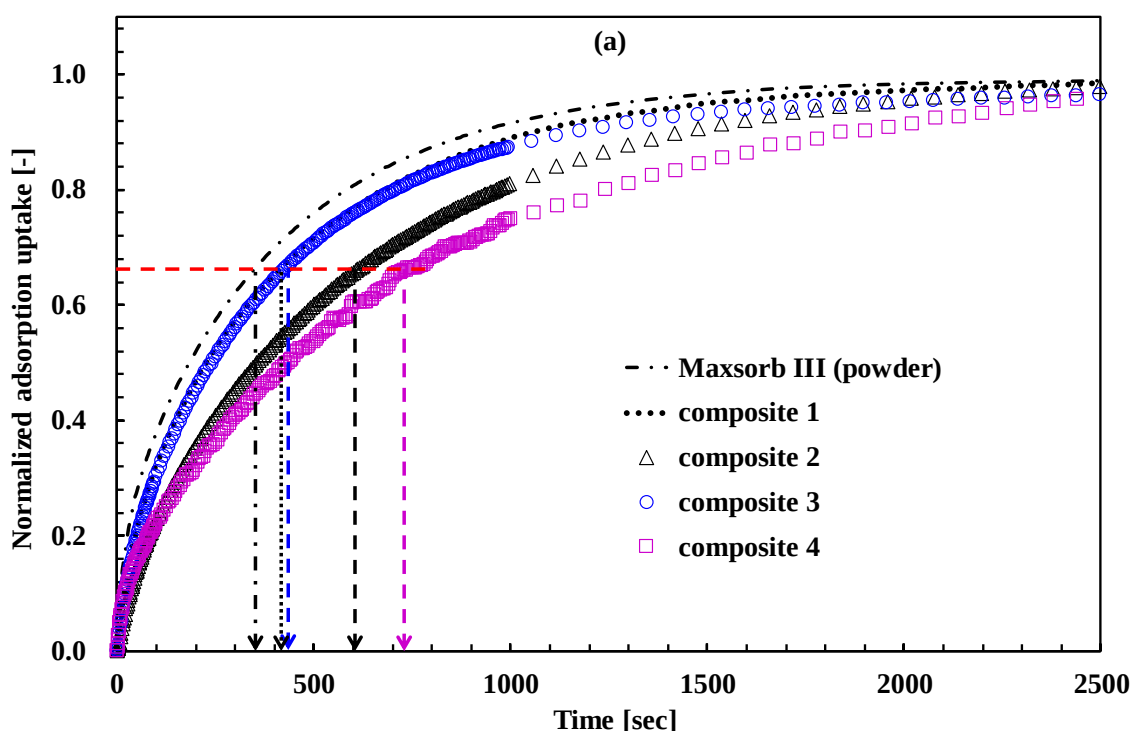


Fig. 4.25 Improvement of effective volumetric (kg m⁻³) adsorption uptake compares to parent adsorbent (Maxsorb III) at evaporator, adsorption and desorption temperatures of 15, 30 and 85°C, respectively.

4.5.2.2 Adsorption kinetics

Adsorption kinetics is one of the important parameters for knowing the dynamic performance of adsorption cooling system [53,148–151]. Loosely packed adsorbent possesses higher adsorption rate compared to its compressed form. Therefore, it is necessary to know the adsorption rate of composite adsorbent. Hence, this study investigates the dynamic adsorption behavior of all composites as well as parent adsorbent. Under the same isothermal condition, the progress of ethanol adsorption with time for all

composites along with Maxsorb III is presented in Fig. 4.26 for all adsorbents. This dynamic ethanol uptake is represented for an adsorption temperature of 30°C and evaporator pressure at 1.8 kPa. As can be seen from normalized uptake plot Fig. 4.26(a), it takes 307, 367, 546, 375, and 670 seconds to reach 63% of the equilibrium uptake of Maxsorb III, composite 1, 2, 3, and 4, respectively. Among all the composites, composite 1 requires the shortest time to reach 63% of its equilibrium value. All GNPs contained composites show almost the same absolute rate up to 200 s as can be seen from Fig. 4.26(b). In addition, absolute ethanol uptake rate of composite 3 is less than composite 2 and 4. Between composite 2 and composite 4, absolute uptake rate is nearly same as their composition ratios are same.



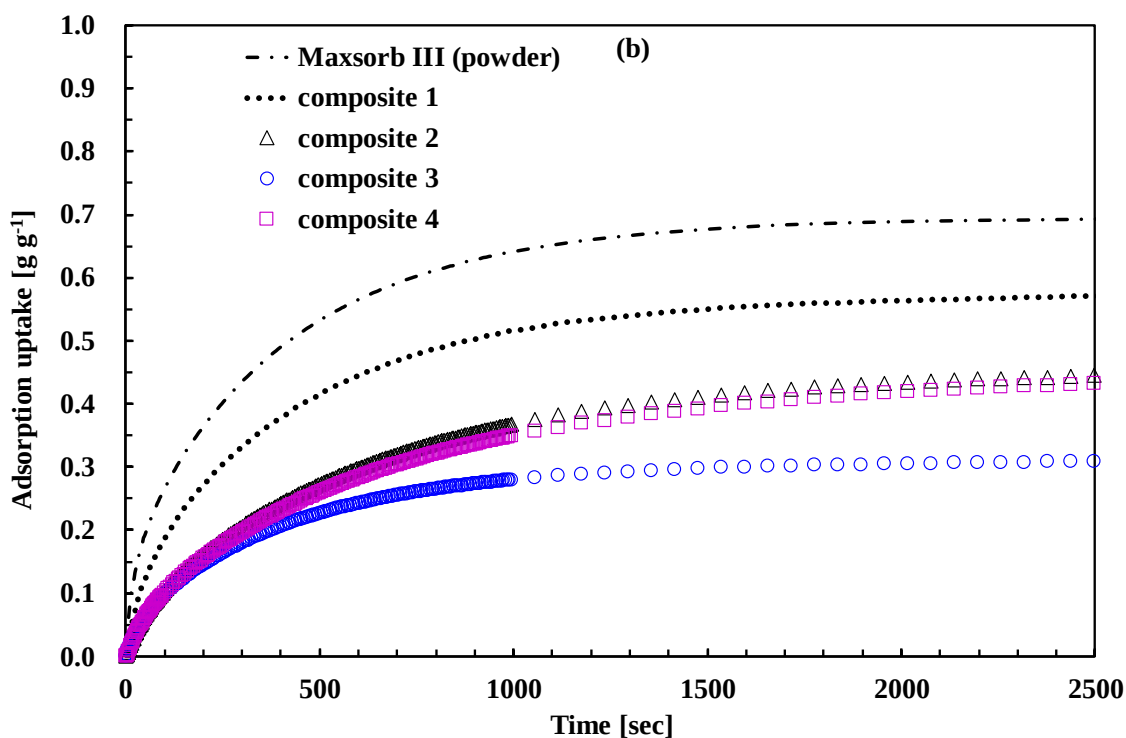


Fig. 4.26 Dynamic adsorption uptake of all studied adsorbents (a) normalized; (b) absolute at adsorption temperature 30°C and evaporator pressure 1.8 kPa.

4.5.3 PAAIL binder based composite

4.5.3.1 Adsorption isotherms

To be our best knowledge, author first time introduced polymerized vinylbenzyltrimethyl ammonium alanine (Poly IL [VBTMA][Ala]) as a binder for the synthesis of composite adsorbent. The detailed of the material characteristics were presented in chapter 3. This chapter illustrates the feasibility study of ethanol adsorption characteristics for AHP application. Equilibrium adsorption uptake versus pressure of the composite A, *i.e.*, Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol pair is presented in Fig. 4.27. It can be seen that adsorption uptake increases with increasing evaporator pressure at given adsorption temperature. It is also found that composite A has the ability to adsorb about 1.11 kg kg⁻¹ of ethanol at adsorption and evaporation temperatures of 303.15 K and 283.55 K, respectively. Dubinin Astakhov (D-A) equation is adopted to fit ethanol adsorption isotherms of composite A/ethanol pair. Numerical values of W_0 , E , and n for composite A/ethanol pair are 1.12 kg kg⁻¹, 126 kJ kg⁻¹ and 1.86, respectively, with ± 2.6 % RMSD.

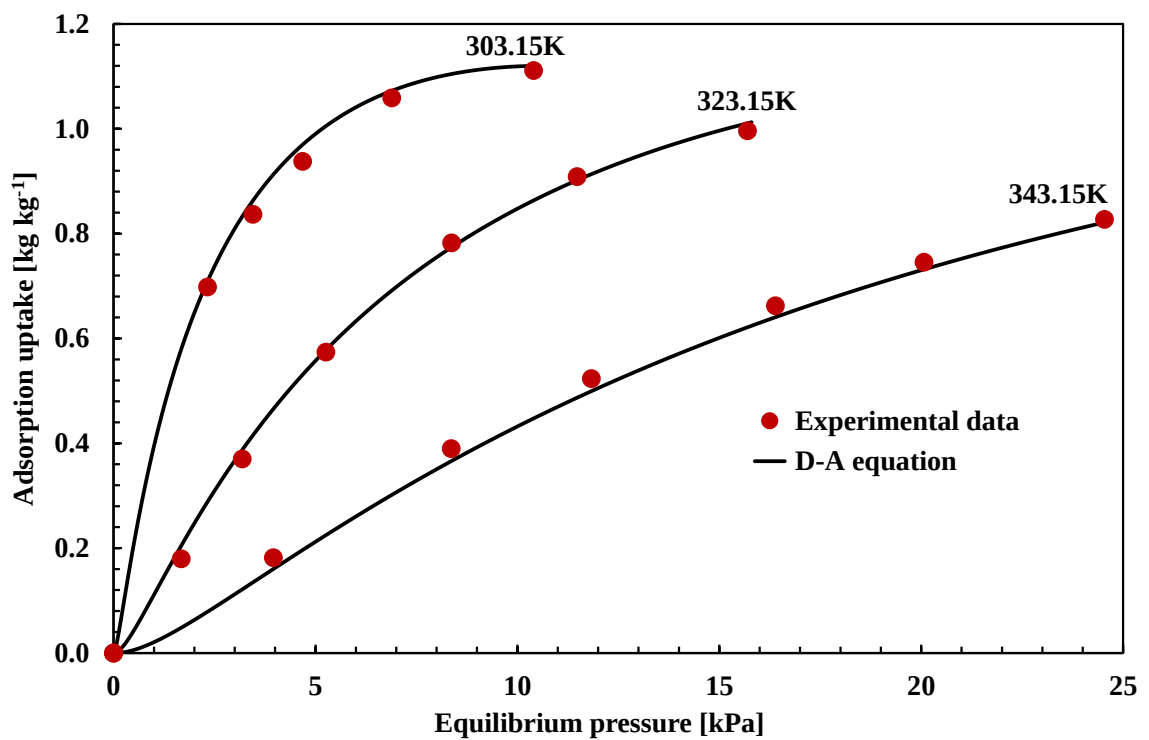


Fig. 4.27 Equilibrium adsorption uptake of ethanol onto composite A: Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%) (fitted with D-A equation).

Fig. 4.28 shows the temporal histories of adsorption uptake and pressure of composite A/ethanol pair for adsorption temperatures of 323.15 K. It can be seen that adsorption uptake increases continuously until the equilibrium condition corresponding to evaporator pressure at each adsorption step. This time-dependent history can be utilized to predict the adsorption kinetics and simulation of designing adsorption heat pump system with the studied pair.

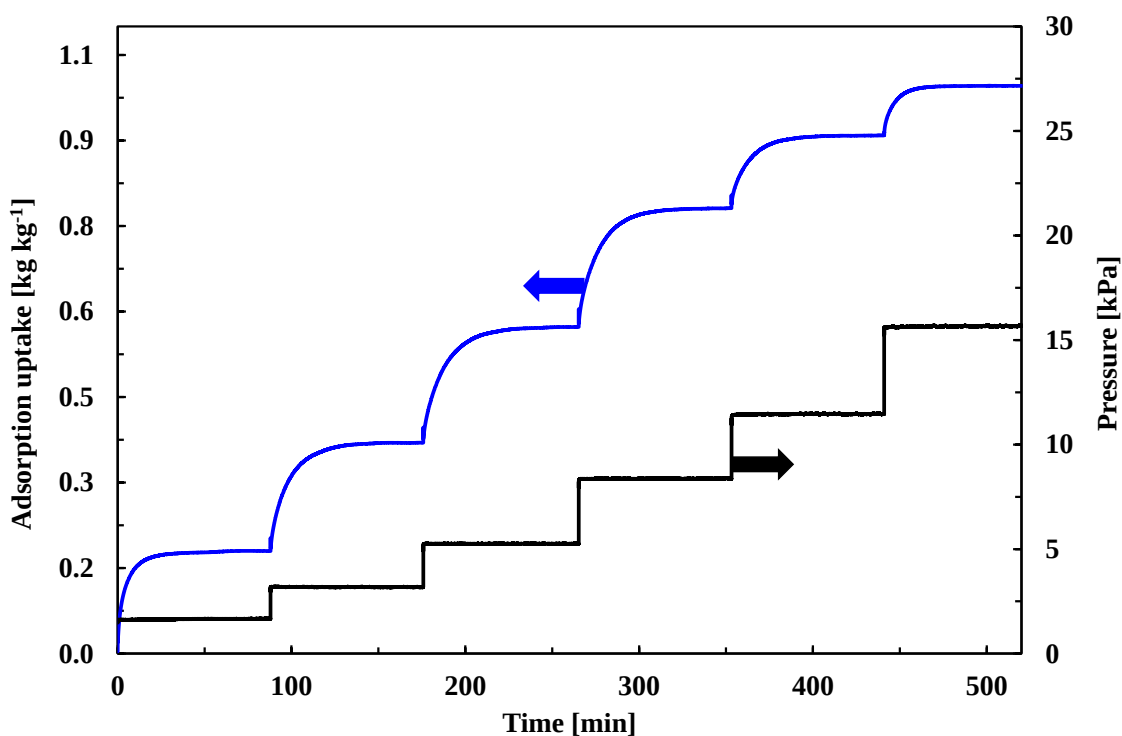


Fig. 4.28 Temporal histories of adsorption uptake and pressure of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol pair at adsorption temperature 323.15 K.

Fig. 4.29 represents the volumetric adsorption uptake of composite A/ethanol pair. The volumetric uptake is estimated using the packing density of composite A and Maxsorb III. The packing density of the developed composite shows 353 kg m^{-3} whilst Maxsorb III possesses 290 kg m^{-3} [46]. It can be seen from Fig. 4.29 that composite A has the ability to adsorb up to 388 kg of ethanol per cube meter at an adsorption temperature of 303.15 K whereas Maxsorb III can adsorb about 348 kg per meter cube at same condition [16].

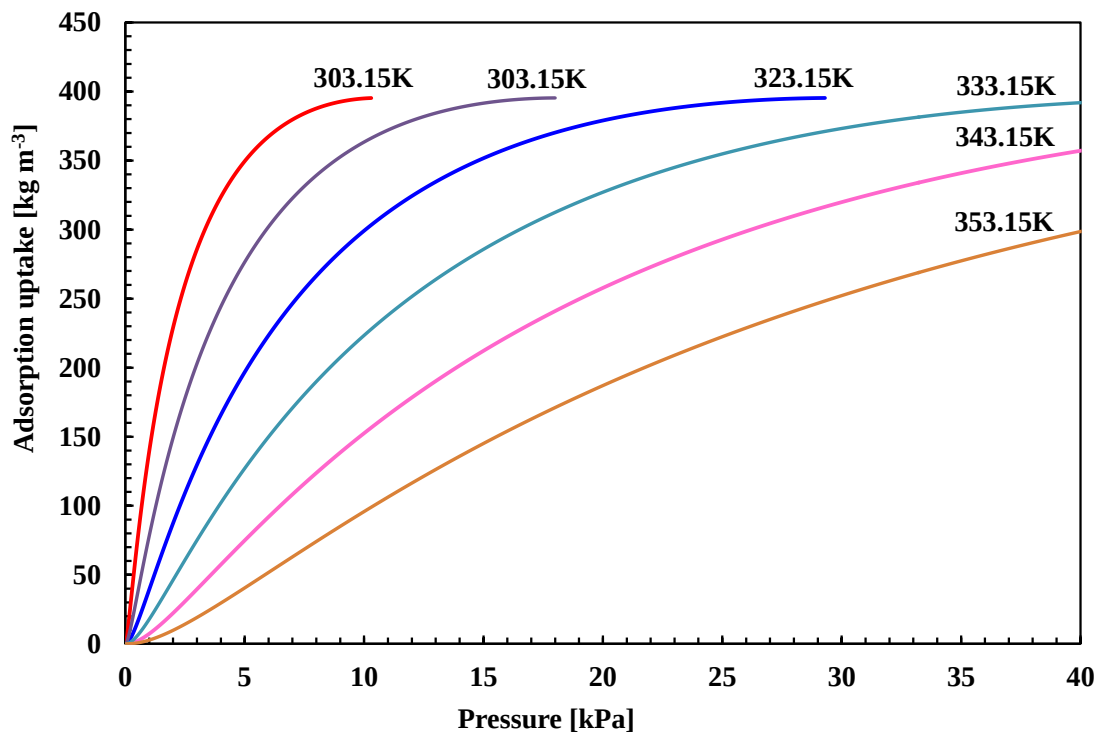


Fig. 4.29 Volumetric adsorption uptake of Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol pair at adsorption temperature ranging from 303.15 K to 353.15 K.

Fig. 4.30 compares the net uptake for the adsorption cooling cycle employing Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol (solid line) and parent material Maxsorb III/ethanol [16] (dashed line) pairs. The evaporation, adsorption, and desorption temperatures have been chosen 280.15K, 303.15K, and 353.15 K, respectively. It is apparent that composite A/ethanol pair (rectangle abcd) shows 22% higher net uptake than that of Maxsorb III/ethanol (rectangle ABCD). Thus, composite using polymerized IL as a binder exhibits a promising potential as an adsorbent for AHP applications. Higher volumetric adsorption uptake has been observed in composite A due to the affinity of refrigerant vapor towards the polymerized IL and high packing density compare to parent material Maxsorb III.

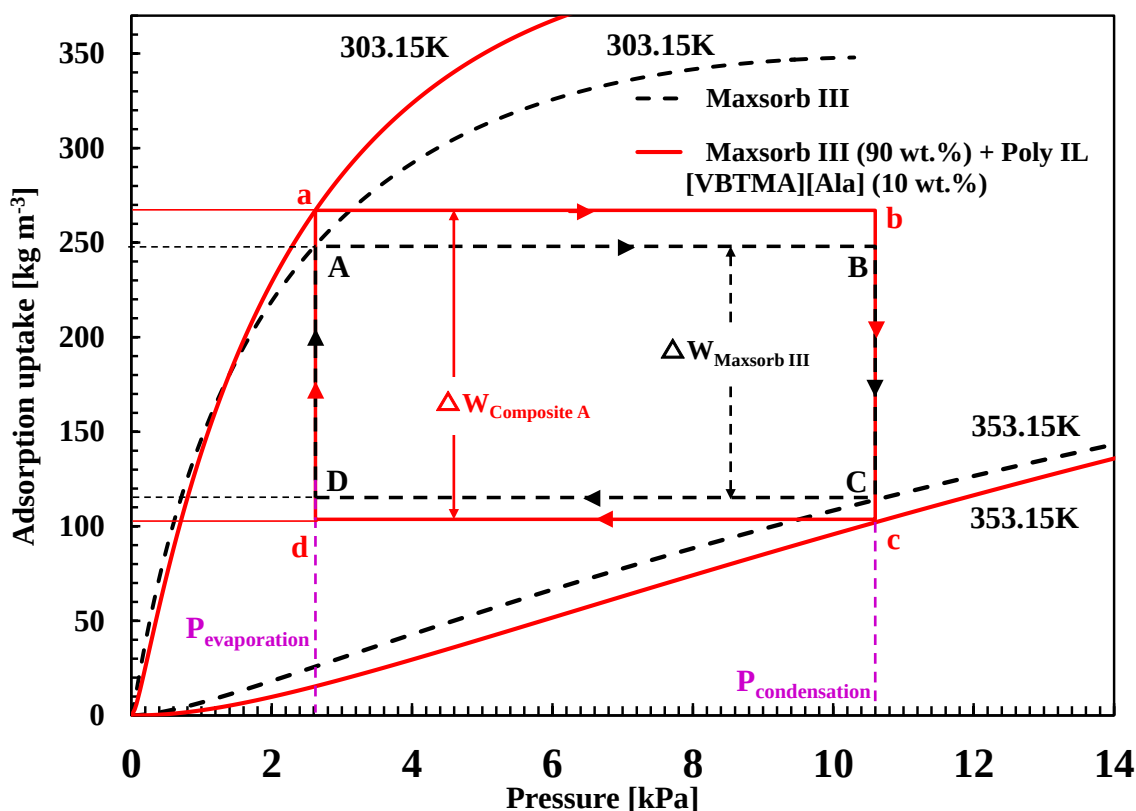


Fig. 4.30 Comparison of adsorption uptake difference of adsorption cooling cycle between composite A: Maxsorb III (90 wt%) + Poly IL [VBTMA][Ala] (10 wt%)/ethanol (solid line) and Maxsorb/ethanol (dashed line) pairs at evaporator, adsorption and desorption temperatures of 280.15, 303.15 and 353.15 K, respectively.

4.6 Conclusions

Biomass-derived ACs: Adsorption uptake and kinetics of ethanol vapor onto WPT-AC (WC600A900K6) and M-AC (MC600A900K6) have been measured gravimetrically at adsorption temperatures between 30 and 70°C. Four popular adsorption isotherm models and two adsorption kinetics equations have been employed to correlate the experimental data. Among the four isotherm models, Dubinin Astakhov (D-A) and Tóth equations agree well with the experimental data for both adsorbents. It is also found that both the ACs show remarkably high adsorption uptake with ethanol. WPT-AC shows the maximum uptake and can adsorb up to 1.9 kg kg^{-1} whilst one kg of M-AC is able to adsorb 1.65 kg of ethanol. Further, the net ethanol uptake for both the biomass-derived-ACs is found to be similar for a real adsorption heat pump and about 35% higher than the net uptake of Maxsorb III/ethanol. The diffusion time constant is estimated for both WPT-

AC/ethanol and M-AC/ethanol pairs. It is observed that WPT-AC/ethanol pair shows faster kinetics than M-AC/ethanol pair. The calculated activation energy of WPT-AC/ethanol and M-AC/ethanol pairs are $309.62 \text{ kJ kg}^{-1}$ and $467.30 \text{ kJ kg}^{-1}$, respectively. Conclusively, the data provided in this present study shows high adsorption capacity of ethanol onto biomass-derived ACs. This study reveals that WPT and mangrove-derived highly porous ACs could be very much promising adsorbent for next generation AHP application from the viewpoint of renewable, low cost, and superior adsorption characteristics.

EG contained AC composites: Adsorption uptakes of ethanol onto prepared consolidated composites have been experimentally investigated. The Dubinin Radushkevich (D-R) and Dubinin Astakhov (D-A) equations have been used to fit adsorption uptake measurement. It is found that 1 kg of consolidated composite (70% Maxsorb III, 20% EG, 10% binder) able to adsorb 0.89 kg of ethanol whilst adsorption capacity of adsorbent composite (50% Maxsorb III, 40% EG, 10% binder) is 0.61 kg kg^{-1} , which are about 74% and 50% of the maximum adsorption uptake of Maxsorb III/ethanol pair, respectively. This is clear evidence that the binder does not sacrifice the adsorption capacity of Maxsorb III of consolidated composites. The volumetric uptake is estimated using the packing density of each composite and found composite A has the ability to adsorb about 325 kg m^{-3} of ethanol at an adsorption temperature of 30°C whilst composite C can adsorb ethanol as high as 380 kg m^{-3} at the same adsorption temperature. In addition, the volumetric uptake difference of composite C/ethanol pair is about 21% higher than that of Maxsorb III/ethanol.

GNPs contained AC composites: Ethanol adsorption isotherms onto the studied composites are fitted with Dubinin Astakhov (D-A) and Tóth models within $\pm 5\%$ RMSD. It is found that equilibrium ethanol adsorption uptake is higher for composite 1 followed by composite 4, 2 and 3. This due to the high BET surface area and pore volume of composite 1. The effective equilibrium volumetric uptake (kg m^{-3}) of all composites show higher compared to Maxsorb III. The highest improvement is observed for composite 2, which is about 23%. The dynamic behavior of ethanol adsorption at temperature 30°C and evaporator pressure at 1.8 kPa is also investigated for all composites and compared with parent adsorbent. The consolidated composite shows a lower absolute rate of ethanol uptake than a parent. However, all GNPs contained composites show almost the same absolute rate. In the viewpoints of all studied aspects (thermal diffusivity/conductivity, instantaneous and equilibrium uptake, packing density and effective volumetric uptake),

this study concludes the composite 3 could be the optimal choice followed by composite 2. Therefore, enhanced thermal conductivity and adsorption characteristics of the synthesized GNPs contained AC composites are important for designing a compact next-generation activated carbon/ethanol based adsorptive cooling systems.

AC composite using PIL binder: Adsorption uptake of ethanol is performed using the thermogravimetric technique at 303.15 K, 323.15 K and 343.15 K with various evaporator pressures. Dubinin Astakhov (D-A) equation is fitted with the experimental data with 2.6% error of regression. The volumetric uptake is estimated using the packing density of PIL composite which has the ability to adsorb about 388 kg m^{-3} of ethanol at an adsorption temperature of 30°C whilst Maxsorb III can adsorb ethanol as high as 348 kg m^{-3} at the same adsorption temperature. For a typical operating condition of AHP system, composite using polymerized IL as a binder showed 22% higher net ethanol uptake than the net uptake of parent material Maxsorb III. Therefore, consolidated activated carbon composite using polymerized IL as a binder shows remarkably high thermal conductivity and desirable affinity for adsorbate in making next generation AHP systems.

Chapter 5

Application to high pressure adsorption systems

A series of synthesized functionally ACs from biomasses, composite adsorbents using expanded graphite (EG) and graphene nanoplatelets (GNPs) for enhancing the thermal conductivity of parent AC were presented in chapter 3. The synthesized adsorbents showed superior porous properties and enhanced thermal conductivity compared to commercial adsorbents. Therefore, in this chapter, the author has been investigated the feasibility of CO₂ adsorption characteristics onto developed adsorbents at various adsorption temperatures and pressures. The high precision gravimetric method based magnetic suspension adsorption measurement unit is employed to measure the adsorption isotherm and kinetics. Finally, the experimental data is analyzed using various adsorption isotherms models.

5.1 Introduction

Utilization of HCFCs and HFCs in heat pump systems leads to an increase in environmental temperature as these have high global warming potential (GWP). According to the Paris agreement in December 2015, the goal is to hold the increase in the global average temperature to well below 2°C. Accordingly, research and development on the utilization of natural and/or alternative refrigerants in heat pump systems have been intensified. Studies showed that adsorption heat pump system could utilize natural or alternative refrigerants and it can be driven by waste heat or solar heat temperature below 100°C [9,44,52,75,76,80,103,152]. Among all natural refrigerants, carbon dioxide (CO₂) offers a number of advantages including excellent thermo-physical properties, high volumetric capacity. Moreover, it is a non-toxic, non-flammable refrigerant having zero ODP and GWP as low as 1. Therefore, it is suitable for adsorption cooling applications where the flammability and toxicity of ammonia and hydrocarbons refrigerants, for example, may be a problem. Besides, adsorption cooling systems using CO₂ as a refrigerant are not limited only to cooling, and air-conditioning applications above 0°C

like those using water, but can also be applied in freezing and ice-making applications. Thermo-physical properties of CO₂ are presented in Table 5.1.

Table 5.1 Thermos-physical properties of carbon dioxide (CO₂).

Chemical formula	CO ₂
Molar mass	44.01 g/mol
Appearance	Colorless gas
Density	1.977 kg/m ³ (gas at 1 atm and 0°C)
Melting point	−56.6°C
Critical point	30.978°C
Critical pressure	7.382 MPa (abs)
Vapor pressure	5.73 MPa (at 20°C)
Latent heat of vaporization	234.5 kJ/kg (0°C)

In this chapter, the adsorption characteristics (isotherm and kinetics) of CO₂ on; i) waste palm trunk and mangrove-derived four AC samples; ii) expanded graphite (EG) contained AC composites; iii) graphene nanoplatelets (GNPs) contained AC composites have been investigated using thermo-gravimetric adsorption measurement unit (TGA). Various adsorption isotherm models are employed to understand the adsorption behavior of CO₂ on studied adsorbents.

5.2 Experiment of adsorption characteristics

5.2.1 Instrumentation

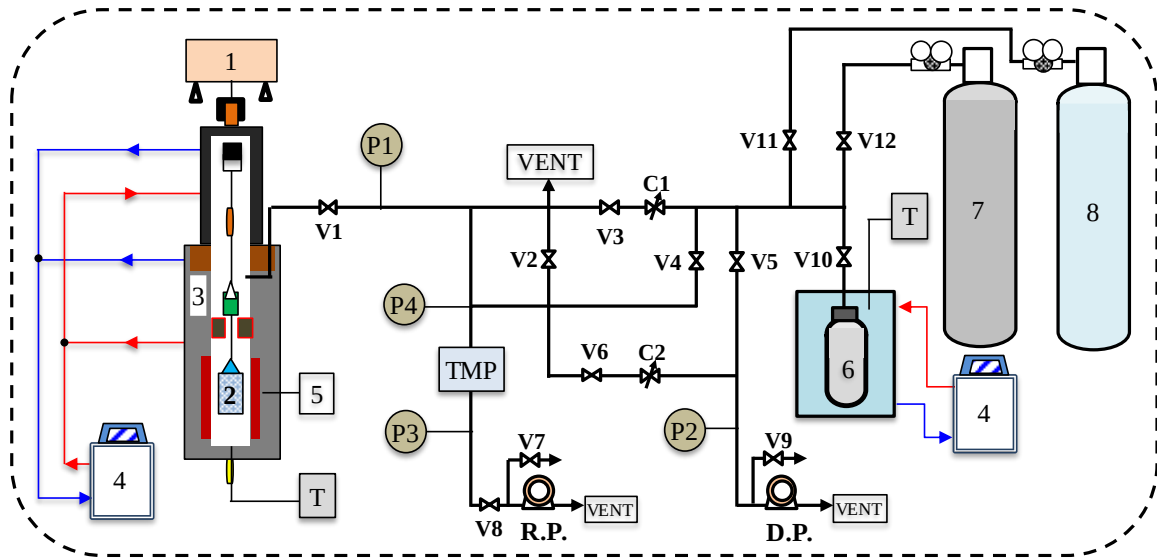
Adsorption isotherms of all studied adsorbent/CO₂ pair have been measured gravimetrically using magnetic suspension adsorption measurement unit (MSB-GS-100-10M) supplied by MicrotracBEL, Japan. Fig. 5.1 shows the schematic diagram of the adsorption isotherms measuring apparatus. It consists of magnetic suspension balance; an evaporator; isothermal circulation oil bath to control the adsorption/evaporation temperatures; isothermal air bath to avoid condensation within the system; a series of vacuum pumps including rotary, diaphragm and turbo-molecular pump; and pressure gauges and thermocouples. The magnetic suspension unit contains a permanent magnet,

sensor code, an electronic control unit. Adsorption amount is measured as weight the gravity created between the electromagnet mounted on the balance and the loading mechanism including a sample hanging from a permanent magnet. To make a measurement under a high temperature and a high pressure without the chance of the balance becoming eroded, the balance section (electromagnet) and the measurement section (load mechanism) are separated from each other by a wall and are not exposed to a measurement atmosphere. It is worth mentioning that buoyancy effect of adsorption quantity measurement is automatically considered by the software. The resolution of magnetic suspension balance is $\pm 10 \mu\text{g}$ to record the sample mass. The weight measurement repeatability of the magnetic balance is $\pm 30 \mu\text{g}$ with relative error $\pm 0.002\%$ of the reading; a 10000 kPa absolute pressure gauge of type Keller PAA-35X is used to measure the pressure with an uncertainty of ± 0.1 of full scale.

5.2.2 Procedure

The magnetic suspension balance unit has been used to measure the adsorption isotherms of studied adsorbent/ CO_2 . Experimental procedure can be described as follows; Firstly, the adsorbent is put into the sample basket and connected to the measuring unit of the system. To remove any adsorbed gas, the sample is then regenerated at 130°C for several hours under vacuum condition for each isotherm. After that, temperature is stabilized for measurement condition. The following technique has been used for the measurements of adsorption isotherms.

- a) To measure the adsorption uptake at low to medium pressure ranges, CO_2 gas is charged into the tube from the CO_2 cylinder and it is then directed to magnetic suspension balance unit. The pressure in the connecting tube is controlled by control valve C1, as shown in Fig. 5.1. The pressure could not go above the saturated vapor pressure of carbon dioxide cylinder at ambient temperature (about 5.7 MPa at 20°C) in this method.
- b) As shown in Fig. 5.1, the liquid reservoir is submerged into a controlled temperature oil bath. In this method, CO_2 is charged into the liquid reservoir and it is directed to the balance unit. Therefore, adsorption pressure is the saturated carbon dioxide pressure in the vaporizer at a set temperature and this method allows measuring pressure up to 7 MPa.



1. Magnetic suspension balance; 2. Sample cell; 3. Circulation oil jacket; 4. Oil bath and circulator; 5. Sheathed heater; 6. Refrigerant container; 7. Isothermal oil bath; 8. CO₂; 9. Helium; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P4: Pressure gauges; C1-C2: Controlled valves; V1-V13: Valves.

Fig. 5.1 Schematic diagram of the experimental apparatus for measuring CO₂ adsorption characteristics.

5.3 Theory of adsorption isotherm models

Adsorption characteristic is crucial for designing adsorption heat pump system. The behavior of equilibrium adsorption uptake of a particular pair entirely depends on adsorbent properties. Therefore, this section introduces popular adsorption isotherm models. Three well-known isotherm models namely Langmuir, Tóth, and modified Dubinin Astakhov (D-A) equations have been employed to fit CO₂ adsorption isotherms of all developed adsorbents as given by equations (5.1) to (5.3), respectively.

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT} P}}{1 + b_0 e^{\frac{Q_{st}}{RT} P}} \quad (5.1)$$

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT}} P}{\left(1 + \left(b_0 e^{\frac{Q_{st}}{RT}} P\right)^h\right)^{1/h}} \quad (5.2)$$

$$q = q_0 \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^n \right] \quad (5.3)$$

Where W is the equilibrium uptake [g g^{-1}], W_0 represents the maximum equilibrium uptake [g g^{-1}], P is the equilibrium pressure [MPa], P_s represents the saturation pressure [MPa], T denotes the adsorption temperature [K], R is the gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], Q_{st} is the isosteric heat of adsorption [kJ mol^{-1}], h is the dimensionless Tóth parameter, n is the exponent of D-A equation, q denotes volumetric adsorption uptake [$\text{cm}^3 \text{g}^{-1}$], and q_0 is the maximum volumetric adsorption capacity [$\text{cm}^3 \text{g}^{-1}$].

The q in the equation (5.3) can be written as;

$$q = WV_m \quad (5.4)$$

The molar volume V_m of adsorbed phase can be calculated using the equation (5.5)

$$V_m = V_t \exp \left(\alpha^* (T - T_t) \right) \quad (5.5)$$

At triple point, the value of parameter V_t of liquid carbon dioxide is $0.84858 \text{ cm}^3 \text{g}^{-1}$. The thermal expansion α^* of the adsorbed gas is 0.0025 K^{-1} as suggested by Saha et al. [17], and Himeno et al. [36]. Amankwah et al. [153] proposed a modified D-A model for estimating pseudo-vapor pressures that are given by the equation (5.6). This methodology introduces a parameter, k , which accounts for interactions in the adsorbate-adsorbent systems. It is a fitting parameter and can be obtained from experimental adsorption isotherm data.

$$P_s = \left(\frac{T}{T_C} \right)^k P_C \quad (5.6)$$

A nonlinear method is used to optimize these model parameters to fit the experimental data for various pressures and temperatures. The root-mean-square deviation (RMSD) value between experimental and calculated adsorption uptake has been obtained according to the equation (5.7) for all studied isotherm models.

$$RMSD = \sqrt{\frac{\sum_{i=1}^N \left(\frac{W_{\text{experimental}} - W_{\text{calculated}}}{W_{\text{experimental}}} \times 100 \right)^2}{N}} \quad (5.7)$$

5.4 Excess and absolute adsorption

The adsorption uptake data obtained from TGA experiment is excess adsorption after buoyancy correction. The absolute adsorption uptake could be attained from excess adsorption [154–156]:

$$W_{\text{absolute}} = W_{\text{excess}} + \rho_{\text{CO}_2} \times V_m \quad (5.8)$$

Where ρ_{CO_2} is the density of CO₂ gas and V_m denotes the pore volume of the adsorbent. Therefore, adsorption isotherm models are fitted after converting excess adsorption uptake (W_{excess}) into absolute adsorption uptake (W_{absolute}).

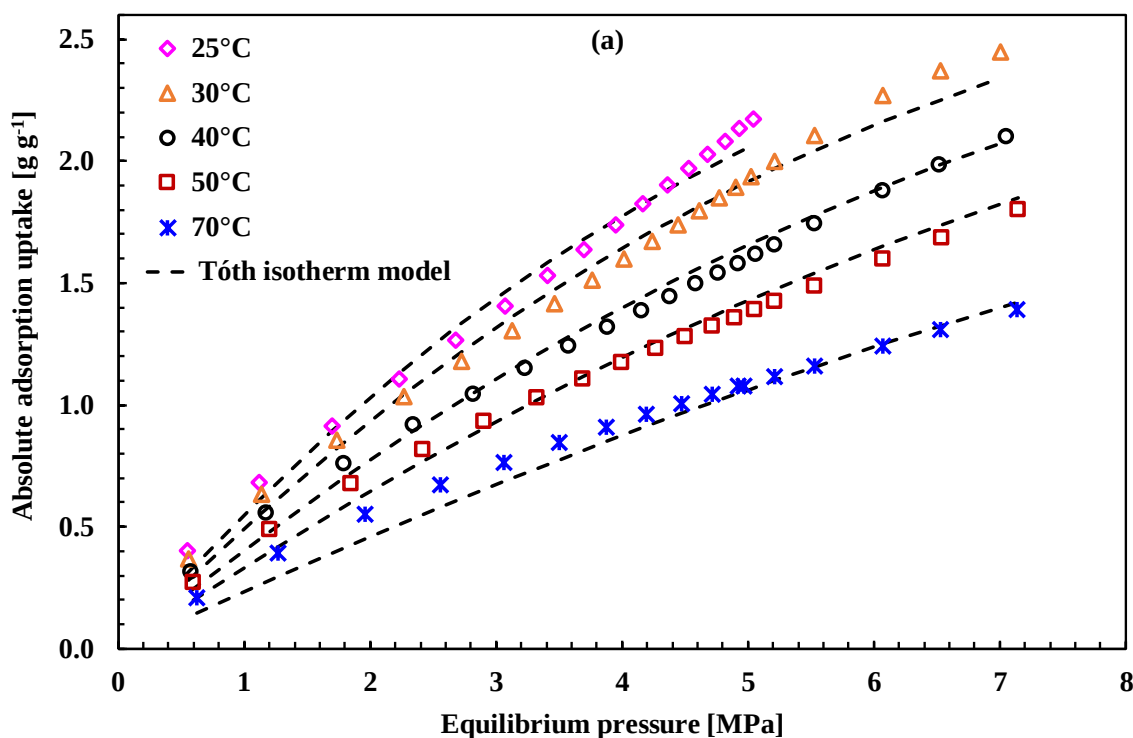
5.5 Biomass-derived ACs/CO₂ pairs

5.5.1 Adsorption isotherm

The porous properties of synthesized biomass-derived activated carbons were discussed in chapter 3. Among series of WPT-AC samples, WC500A900K6 and WC600A900K6 are selected for investigation of CO₂ adsorption and named as WC500 and WC600, respectively. MC500A900K6 and MC600A900K6 are chosen among mangrove-derived AC samples for further investigation and named as MC500 and MC600, respectively in this chapter. Fig. 5.2 and Fig. 5.3 illustrate the equilibrium absolute adsorption uptake of WC500A900K6/CO₂ and WC600A900K6/CO₂ pair, respectively at adsorption temperatures 25 to 70°C with pressure up to 7 MPa. For both pairs, it is found that Tóth and modified D-A model fit well with the experimental data within ±5% root-mean-square deviation (RMSD). Fig. 5.2 (a) and (b) show the fitted Tóth and modified D-A model with experimental data for WC500/CO₂ pair, respectively. In addition, Fig. 5.3 (a) and (b) represent the fitted Tóth and modified D-A model with experimental data for WC600/CO₂ pair, respectively.

The similar analysis has been also done for MC500/CO₂ and MC600/CO₂ pairs are shown in Fig. 5.4 and Fig. 5.5, respectively with the fitted isotherm model. Estimated isotherm parameters of the studied models for all pairs have been summarized in Table 5.2. It is important to mention that synthesized biomass-derived ACs are very promising

for CO₂ adsorption as they possess high adsorption uptake. The maximum volumetric absolute uptake is found about 2.6 cm³ g⁻¹ for WC500/CO₂ pair followed by 2.4 cm³ g⁻¹, 2.3 cm³ g⁻¹, and 2.1 cm³ g⁻¹ for MC500, WC600, and MC600/CO₂ pair, respectively. However, Maxsorb III/CO₂ pair only shows the volumetric absolute uptake 1.5 cm³ g⁻¹. It should be highlighted that biomass-derived all four AC samples show very high adsorption uptake which is about 40% to 73% enhanced uptake compared to Maxsorb III/CO₂ pair. This reason behind this that all synthesized biomass-derived ACs possess very high pore volume. Furthermore, isosteric heat of adsorption (Q_{st}) is lower for biomass-derived ACs that is good for cooling applications. Therefore biomass-derived ACs are very promising for CO₂ based adsorption heat pump systems.



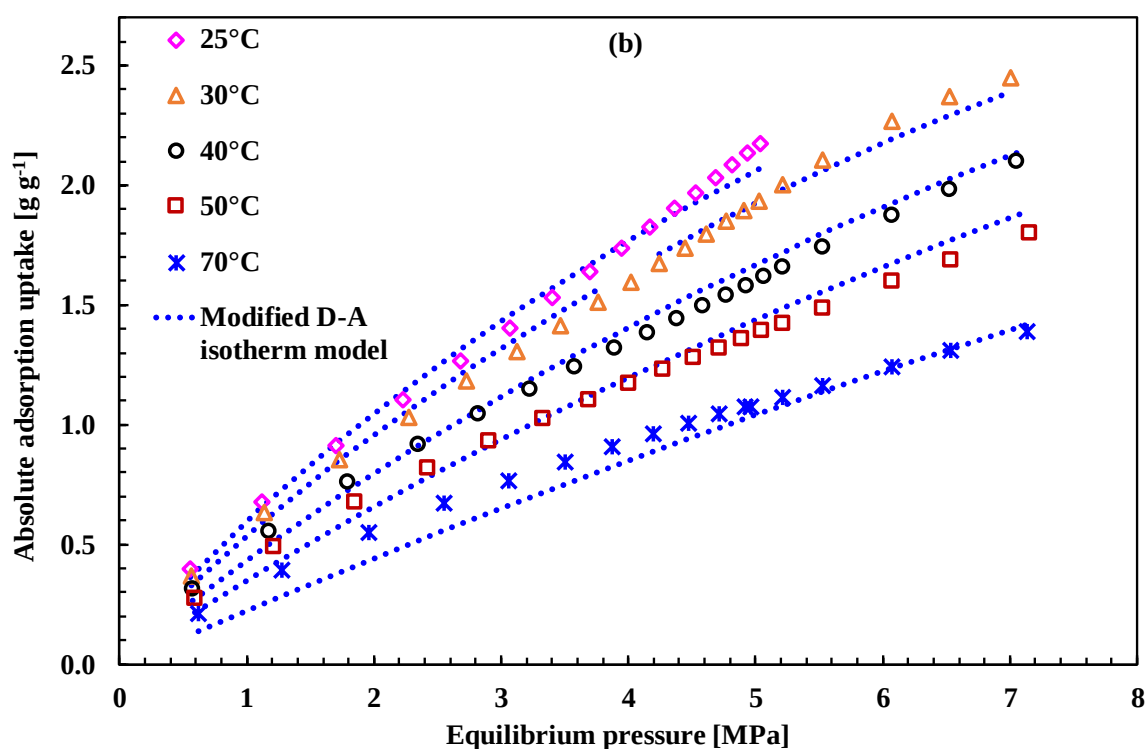
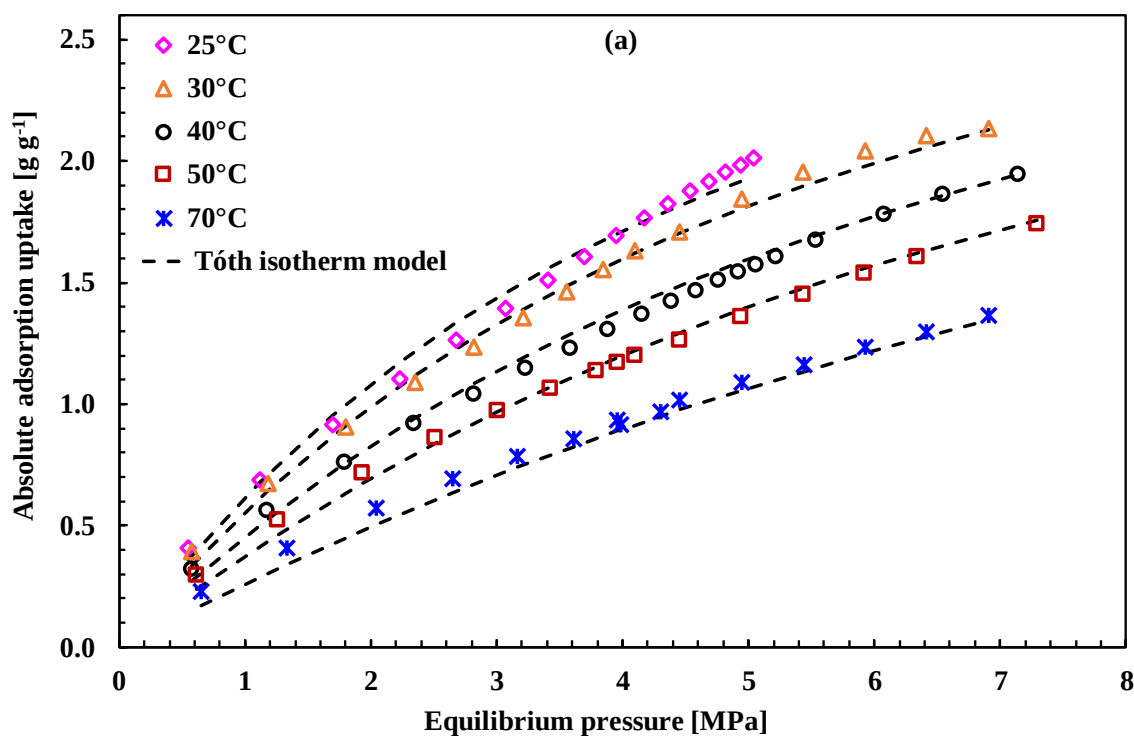


Fig. 5.2 Adsorption isotherms of WC500 (WC500A900K6/CO₂ pair (data are fitted with (a) Tóth and (b) modified D-A model).



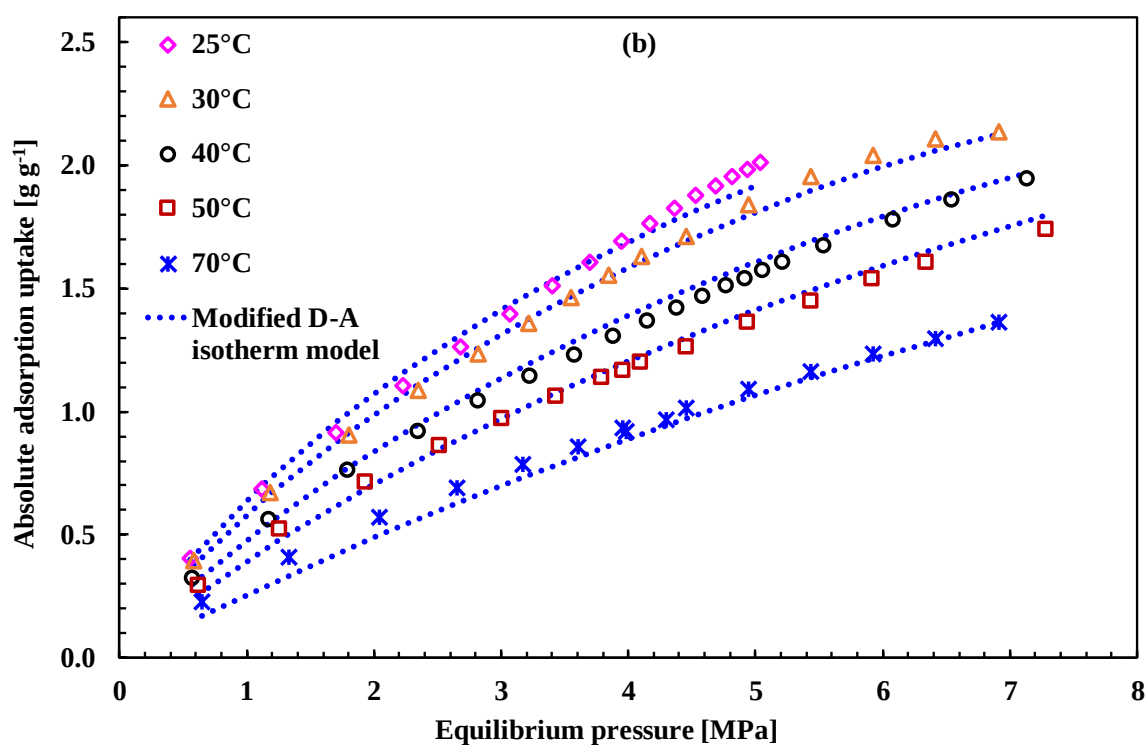
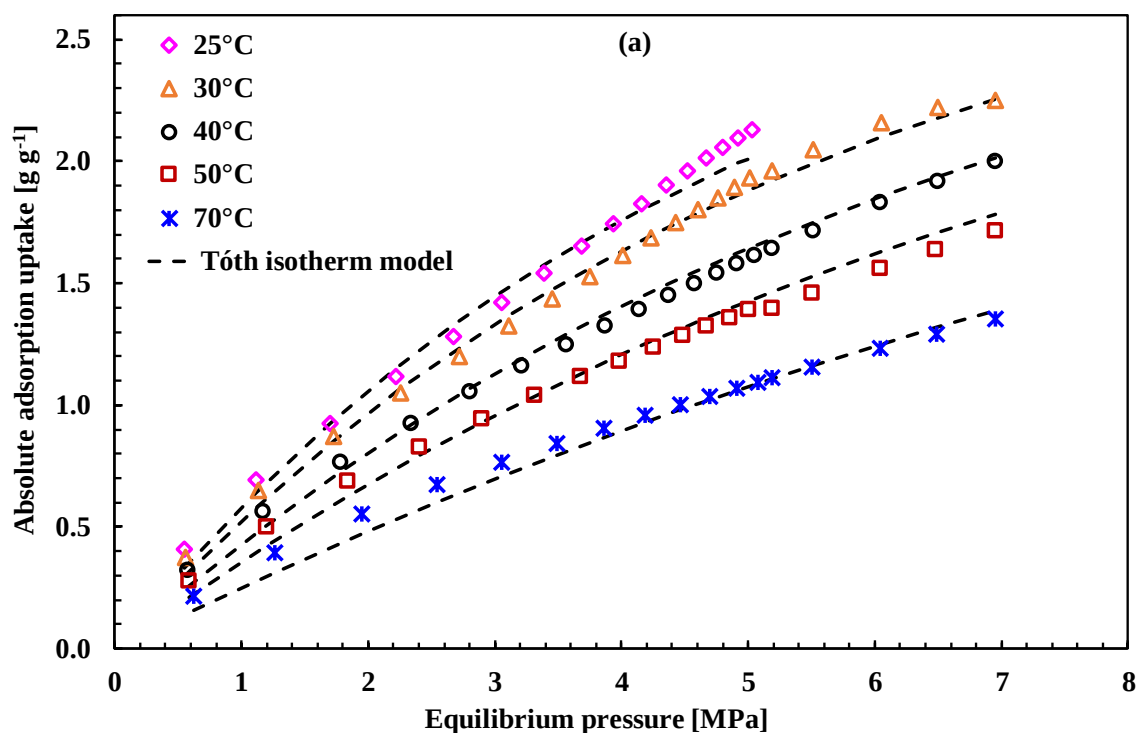


Fig. 5.3 Adsorption isotherms of WC600 (WC600A900K6)/CO₂ (data are fitted with (a) Tóth and (b) modified D-A model).



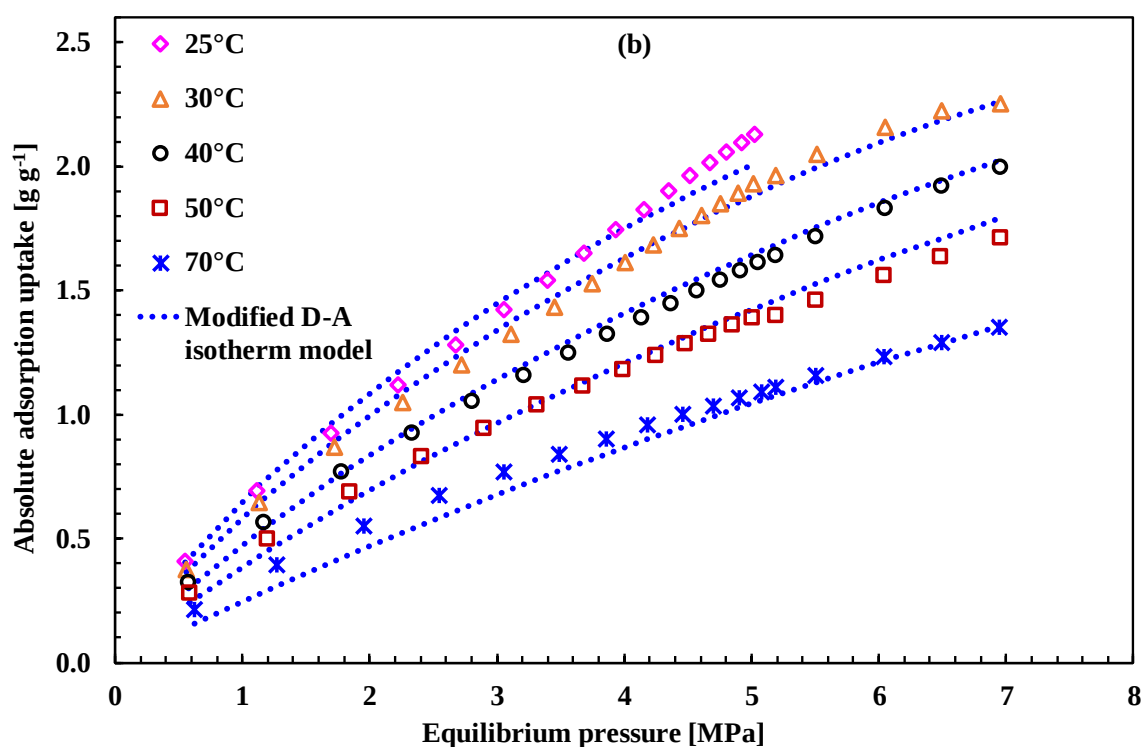
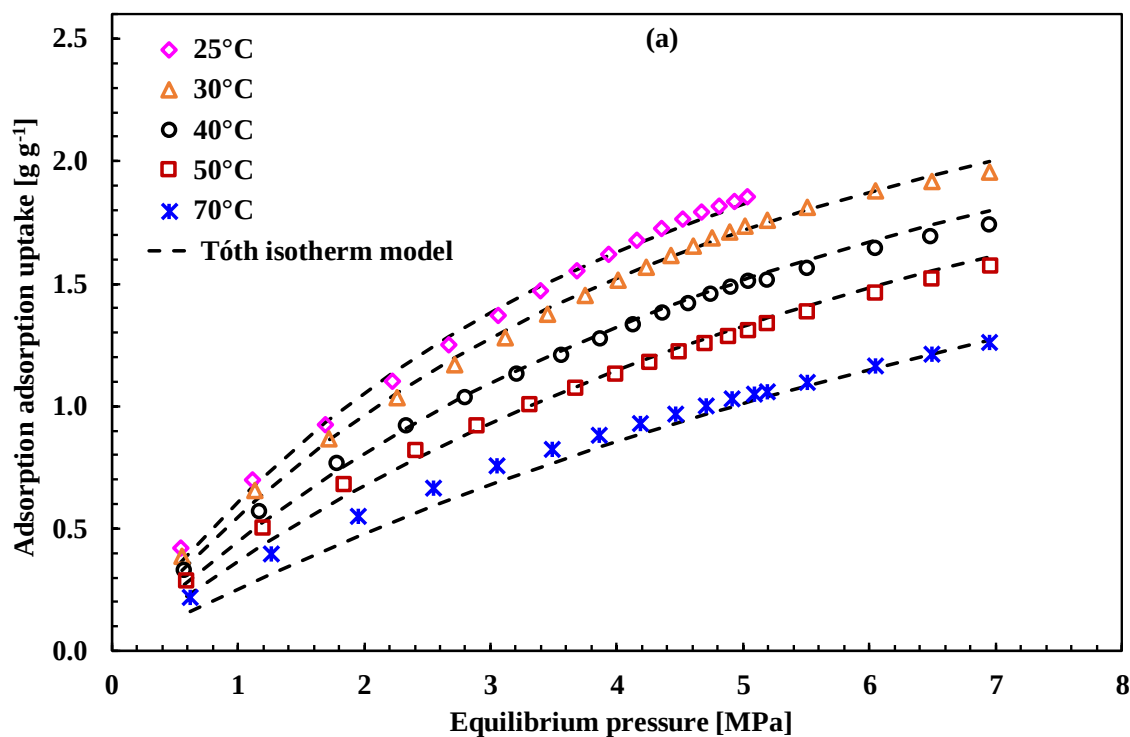


Fig. 5.4 Adsorption isotherms of MC500 (MC500A900K6/CO₂ pair (data are fitted with (a) Tóth and (b) modified D-A model).



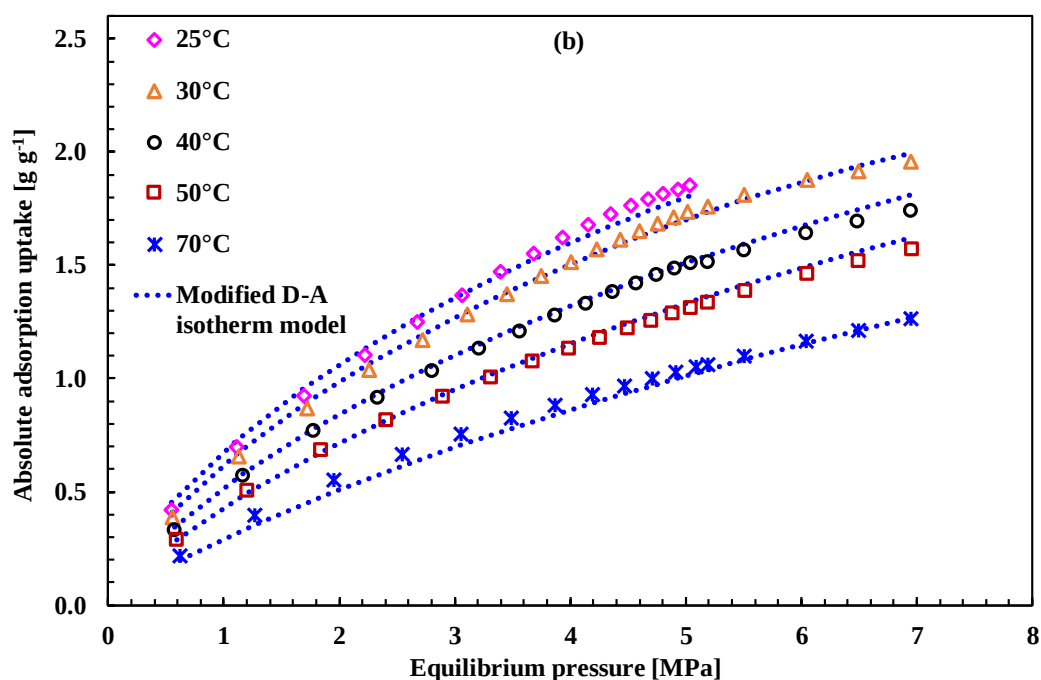


Fig. 5.5 Adsorption isotherms of MC600 (MC600A900K6)/CO₂ (data are fitted with (a) Tóth and (b) modified D-A model).

Table 5.2 Fitting parameters of the studied isotherm models for biomass-derived ACs/CO₂ pairs.

Model	Fitting parameters	WPT-AC (C500)	WPT-AC (C600)	M-AC (C500)	M-AC (C600)
Modified D-A	q_0 [cm ³ g ⁻¹]	2.5599	2.2775	2.4213	2.1321
	E [J mol ⁻¹]	3466.43	3995.67	3809.68	4322.67
	k [-]	4.537	4.437	4.776	4.749
	n [-]	1.12	1.20	1.15	1.15
	RMSD [%]	5.534	4.118	4.786	2.975
Tóth	W_0 [g g ⁻¹]	3.90	3.50	3.85	3.20
	Q_{st} [J mol ⁻¹]	16653.64	17685.23	16954.41	18473.66
	h [-]	1.4927	1.1743	1.2912	1.1286
	b_0 [MPa ⁻¹]	1.762×10^{-4}	1.577×10^{-4}	1.732×10^{-5}	1.290×10^{-4}
	RMSD [%]	5.543	3.967	4.723	3.348

The effective or net adsorption uptake (ΔW) is defined as the difference between the maximum and minimum uptake at the particular operating condition. It is a crucial parameter for getting the cooling effect. In this study, effective uptake of biomass-derived ACs/CO₂ pairs has been compared with several literature studies on evaporation, adsorption, and desorption temperature are 15, 28, and 85°C, respectively. It is found ΔW is very high compared to any other adsorbents/CO₂ pairs. The ΔW values for all studied pairs together with literature are furnished in Table 5.3. It is also seen that higher surface area and pore volume attributes for enhancing ΔW of studied biomass-derived ACs/CO₂ pair. Fig. 5.6 shows the ΔW variation with the changes of the pore volume of the adsorbent. It is found that usually effective uptake increase with the increase of pore of adsorbent. Importantly, synthesized biomass-derived ACs/CO₂ pairs lie in the top of the figure, which is the current benchmark.

Table 5.3 Comparison of effective uptake of the present study with numerous pairs of literature data at evaporation, adsorption, and desorption temperature are 15, 28 and 85°C, respectively.

Adsorbent/CO ₂	Effective uptake, ΔW [g g ⁻¹]	Surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore size [nm]	Reference
WPT-AC (C500)	0.81	2848	2.87	1.96	Present study
WPT-AC (C600)	0.75	2927	2.51	1.68	Present study
M-AC (C500)	0.81	2911	2.68	1.81	Present study
M-AC (C600)	0.72	2924	2.18	1.47	Present study
Maxsorb III	0.46	3045	1.70	1.12	Jribi et al. [18]
A-20 (ACF)	0.27	2000	1.03	2.16	Saha et al. [52]
Maxsorb III	0.60	3150	1.70	2.0	Saha et al. [52]
Composite	0.39	2000	1.094	1.0 ~ 3.5	Pal et al. [135]
Maxsorb	0.24	3250	1.79	-	Himeno et al. [36]
Norit R1 Extra	0.09	1450	0.47	-	Himeno et al. [36]
BPL	0.08	1150	0.43	-	Himeno et al. [36]
A10 fiber	0.07	1200	0.59	-	Himeno et al. [36]
Activated carbon A	0.07	1207	0.54	-	Himeno et al. [36]
Norit RB3 (steam activated rod) (AC1)	0.16	987.04	0.51	2.10	Singh et al. [39]
Norit Darco (100 mesh size) (AC2)	0.13	876.45	0.73	3.33	Singh et al. [39]
Norit Darco (12 × 20 US mesh size) (AC3)	0.09	462.67	0.50	4.28	Singh et al. [39]
CSAC (Coconut shell based activated carbon)	0.10	804.02	0.43	1.76	Singh et al. [38]

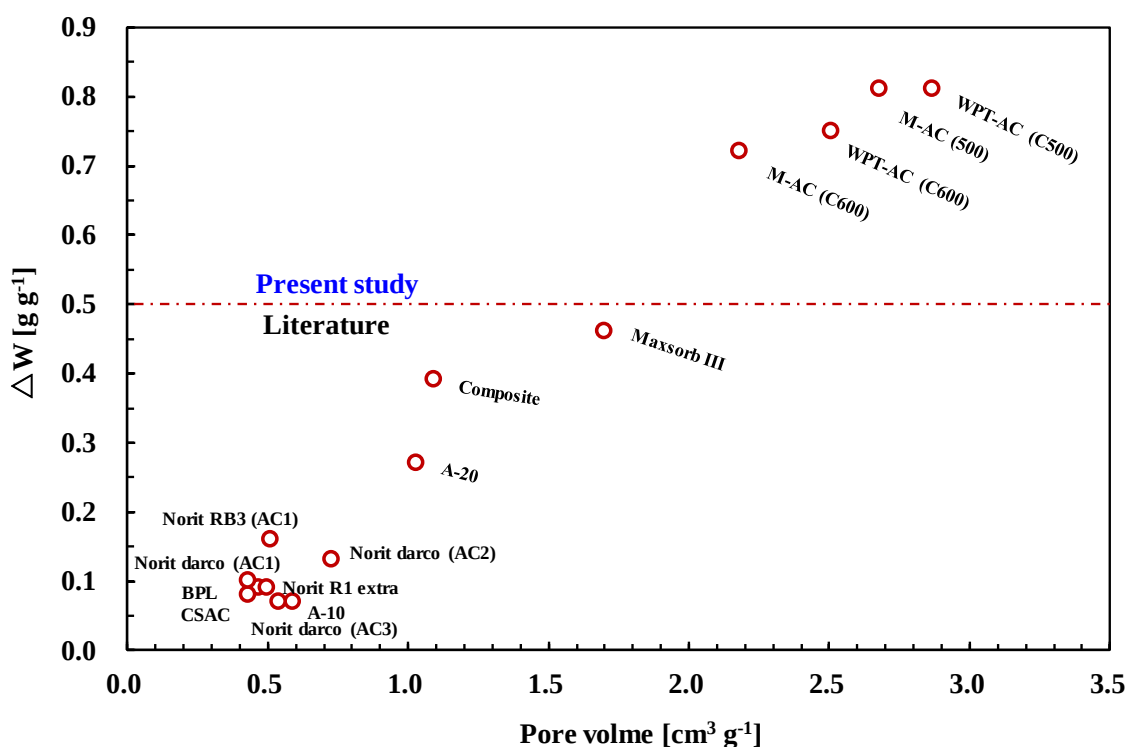


Fig. 5.6 Effective uptake (ΔW) as a function of adsorbent pore volume.

Fig. 5.7 illustrates the ΔW improvement of biomass-derived ACs/ CO_2 pairs with the comparison of Maxsorb III/ CO_2 and Norit RB3/ CO_2 at evaporation, adsorption, and desorption temperature are 15, 28 and 85°C. It is found that all biomass-derived ACs shows a high percentage of ΔW improvement compared to Maxsorb III and Norit RB3. The highest improvement is found 176% and 506% compared to Maxsorb III and Norit RB3, respectively.

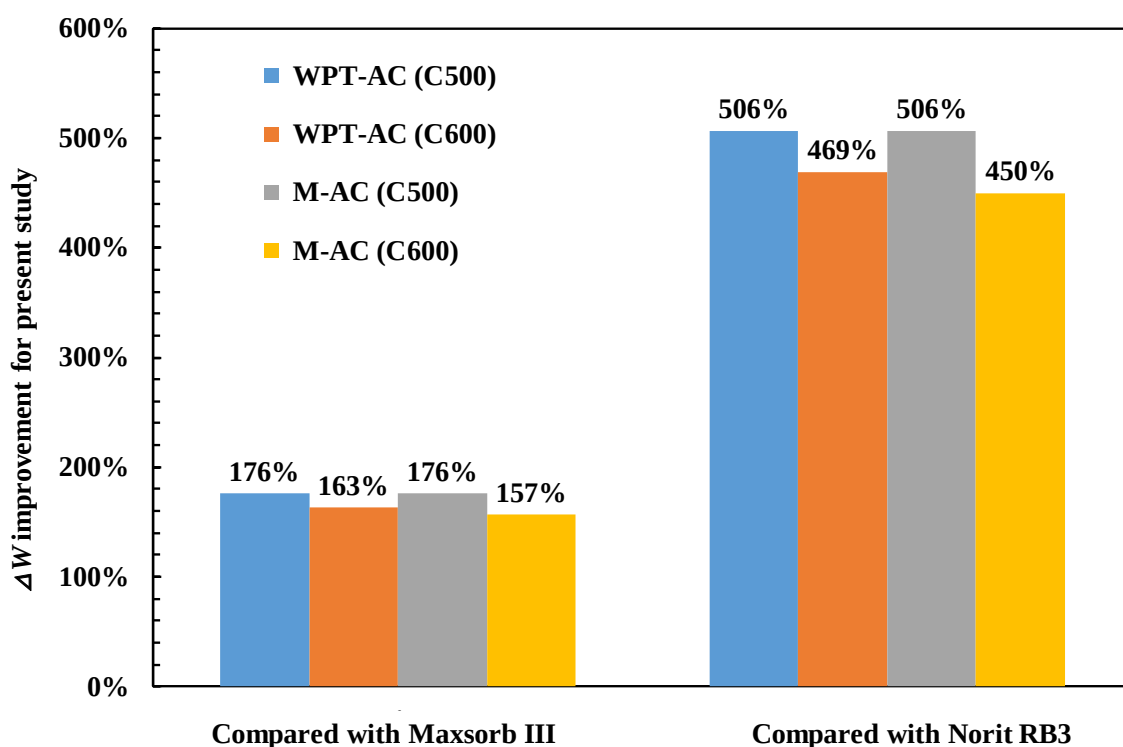


Fig. 5.7 ΔW improvement of biomass-derived ACs with the comparison of Maxsorb III and Norit RB3 at evaporation, adsorption, and desorption temperature are 15, 28 and 85°C.

5.5.2 Adsorption kinetics

Normalized adsorption uptake as a function of time for all biomass-derived ACs/CO₂ pairs along with Maxsorb III/CO₂ pair is shown in Fig. 5.8. There is no significant difference in time constant for reaching 63% of its equilibrium adsorption uptake among the WPT-AC and M-AC samples, as can be seen from the figure. Moreover, biomass-derived ACs show slightly faster adsorption than Maxsorb III. Since CO₂ is higher pressure adsorbate gas. As a result, all samples reach their equilibrium value very rapidly. However, absolute uptake rate of CO₂ onto all ACs are different because of their different adsorption capacity. The absolute uptake rate of Maxsorb III/CO₂ is less than any other pairs as shown in figure Fig. 5.9. Therefore, the absolute adsorption rate of CO₂ onto biomass-derived ACs is higher than Maxsorb III and among them, WPT-AC (C600) is the highest followed by WPT-AC(C500), M-AC (C500) and M-AC (C600) at a given time.

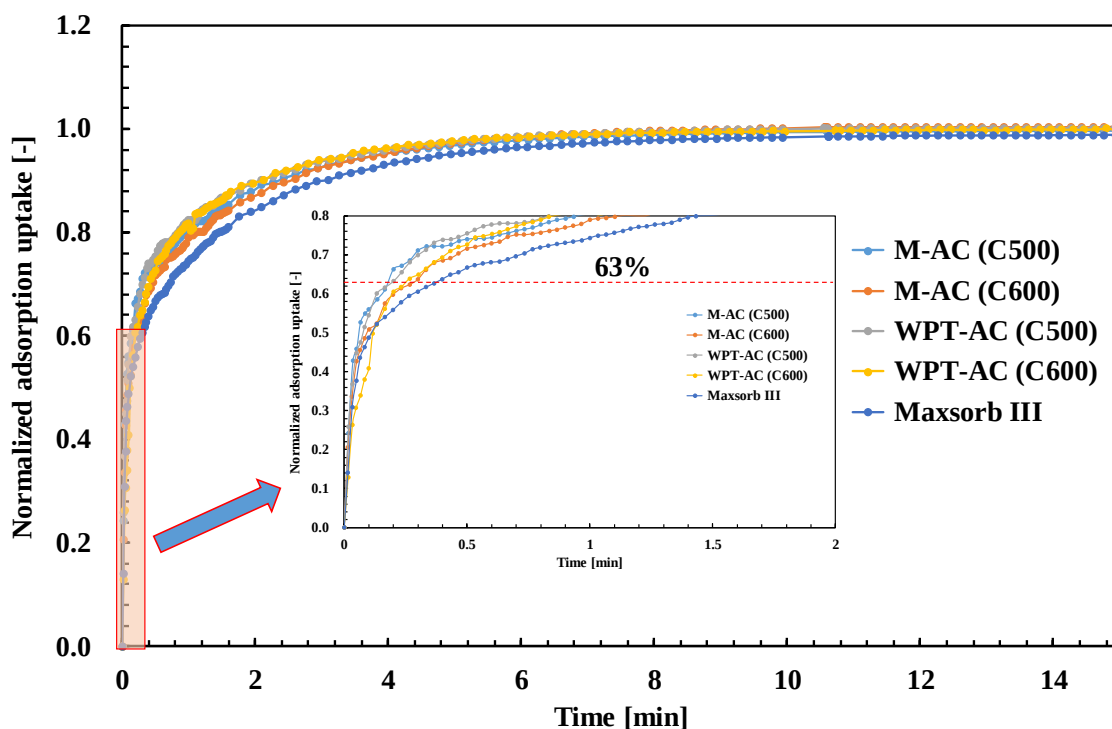


Fig. 5.8 Normalized adsorption uptake as a function of time for all biomass-derived ACs/CO₂ pairs along with Maxsorb III/CO₂ pair at adsorption temperature 30°C and evaporator pressure about 560 kPa.

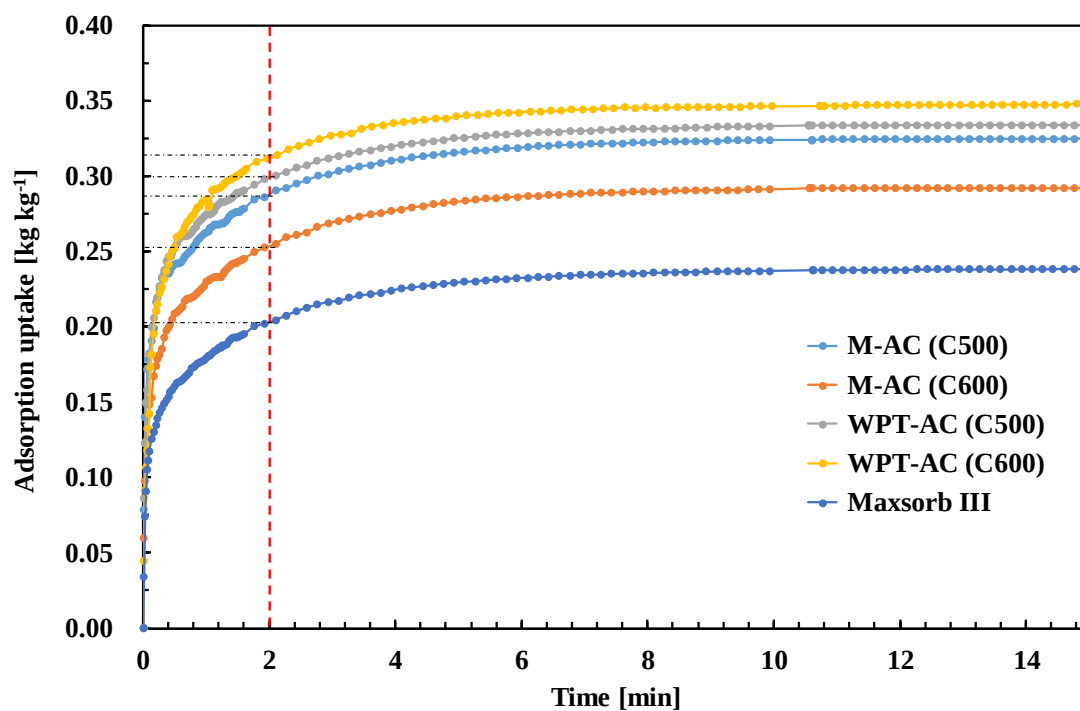


Fig. 5.9 Instantaneous absolute uptake of all biomass-derived ACs/CO₂ pairs along with Maxsorb III/CO₂ pair at same condition presented in Fig. 5.8.

5.6 Composites/CO₂ pairs

5.6.1 EG contained composites/CO₂ pairs

In chapter 3 discussed the properties of synthesized expanded graphite (EG) contained composites. Among them, composite C (70% Maxsorb III, 20% EG, 10% binder) has been chosen for CO₂ adsorption characteristics because it could be a suitable combination from the viewpoints of porous properties and thermal conductivity. The CO₂ adsorption experiments have been conducted at temperatures of 30, 50, 70°C and pressure up to 7 MPa using magnetic suspension adsorption measurement unit. Figs. 5.10 –5.12 represent a good agreement between the experimental and predicted adsorption uptake using Langmuir, modified D-A equation, and Tóth, respectively. The marker points in the figures show the measured uptakes whereas solid lines indicate the fitted data with studied adsorption models. It can be seen from Figs. 5.10 –5.12 that the adsorption uptake increases with the increase of equilibrium pressure. It is also observed from the experimental data that the maximum adsorption uptake of CO₂ onto studied composite adsorbent is about 1 kg of CO₂ per kg of adsorbent. Isotherm parameters of the studied adsorption isotherm models have been optimized to fit the measured data for temperatures 30, 50, and 70°C. The numerical value of isotherm parameters has been furnished in Table 5.4. It can be mentioned that among the three isotherm models, Tóth model fits well with the experimental isotherms. The effect of k parameter on adsorbed volume W versus adsorption potential A is shown in Fig. 5.13. For k equal to 4.886, a single characteristic curve is obtained for adsorption temperatures 30, 50, and 70°C, which indicates that characteristic energy is independent of temperature. A similar observation was also reported by Saha et al. [52] and Himeno et al. [36]. A comparison between present study, Saha et al. [52] and Himeno et al. [36] of adsorption uptake of CO₂ onto Maxsorb III in kilogram per cubic meter have been depicted in Fig. 5.14. In this comparison packing density of prepared composite adsorbent is found to be 480 kg m⁻³, whilst Maxsorb III powder is found to be 290 kg m⁻³ [46]. It is noticed that present study shows higher adsorption capacity of CO₂ per cubic meter of adsorbent. In addition, El-Sharkawy et al. [46] reported that consolidated composite adsorbent with similar composition (70% Maxsorb III, 20% EC500, and 10% PVA) possess higher thermal conductivity compared to Maxsorb III powder.

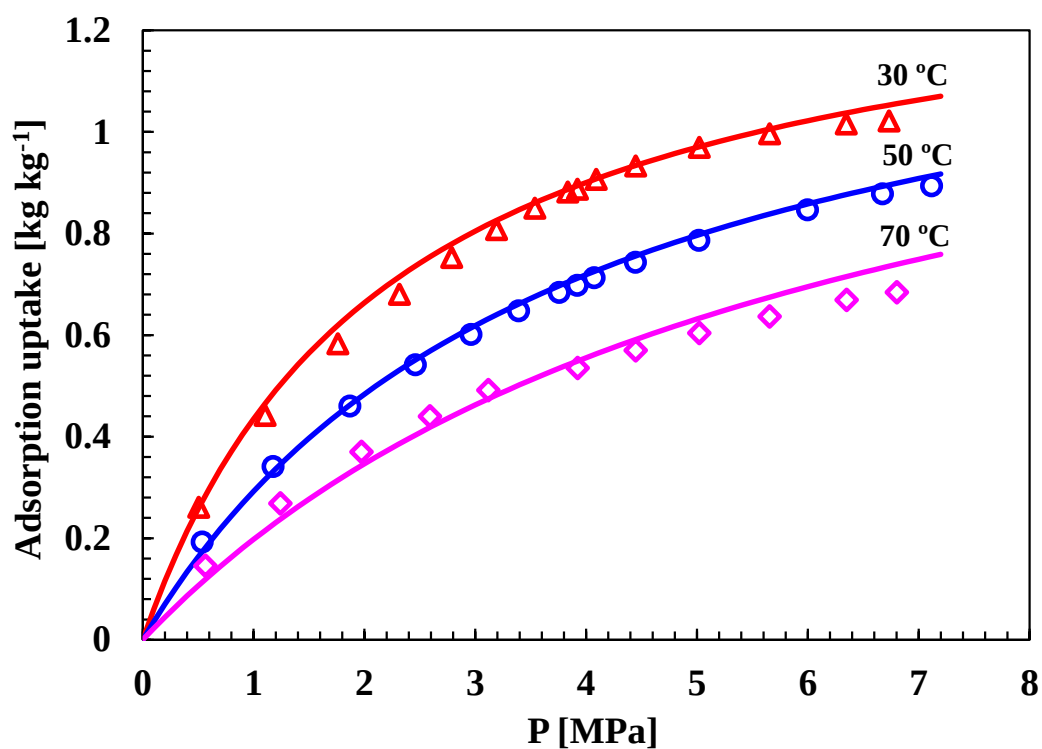


Fig. 5.10 Adsorption isotherms of CO₂ onto composite C (data are fitted with Langmuir model).

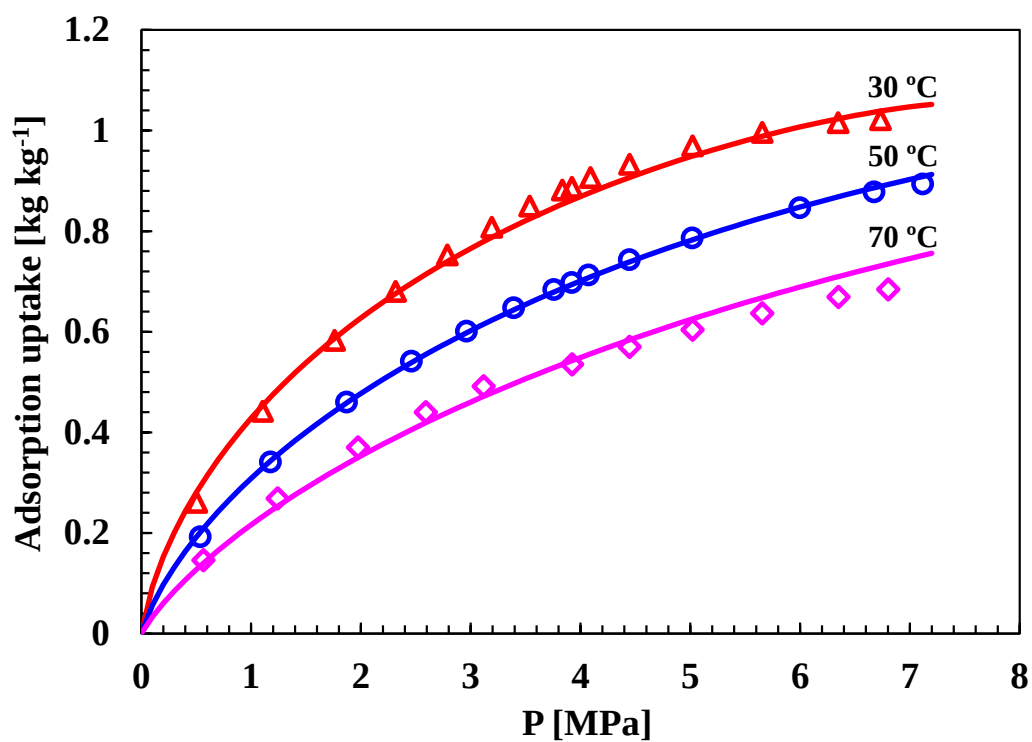


Fig. 5.11 Adsorption isotherms of CO₂ onto composite C (data are fitted with modified Dubinin-Astakhov (D-A) equation).

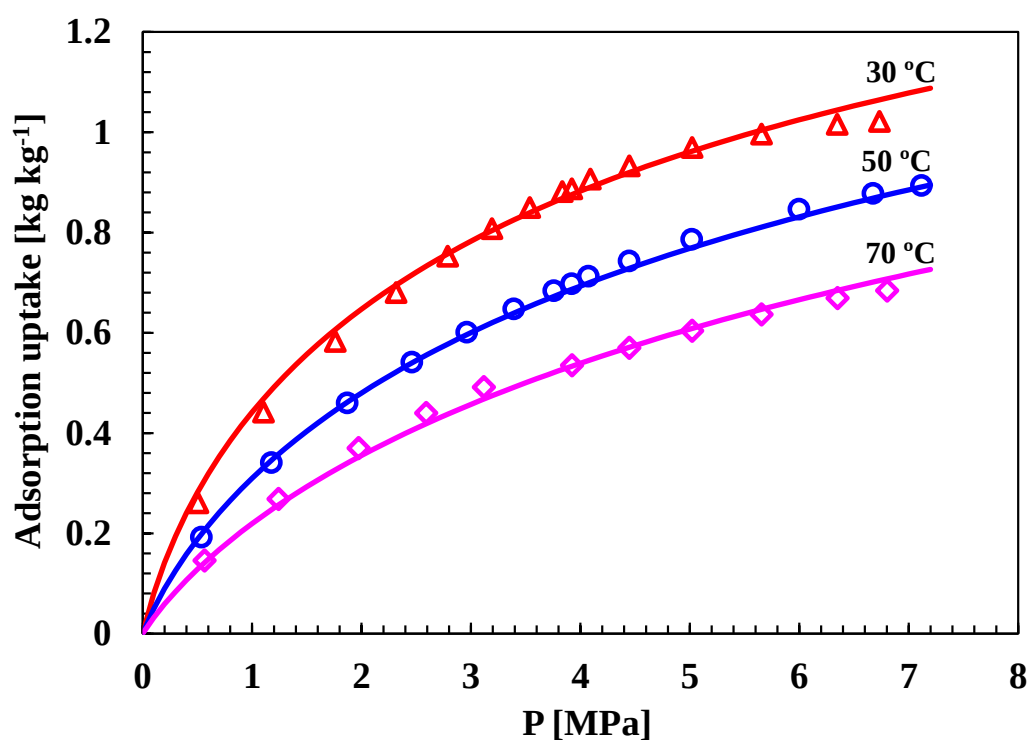


Fig. 5.12 Adsorption isotherms of CO₂ onto composite C (data are fitted with Tóth model).

Table 5.4 Fitting parameters of the isotherm models for CO₂ adsorption onto the composite adsorbent.

Isotherm parameters	Langmuir	Tóth	Modified D-A
W_0 [kg kg ⁻¹]	1.4	2.05	-
b_0 [MPa ⁻¹]	7.90×10^{-5}	6.67×10^{-5}	-
Q_{st} [kJ mol ⁻¹]	21.8	22.5	-
h [-]	-	0.6	-
k [-]	-	-	4.844
q_0 [cm ³ g ⁻¹]	-	-	1.109
E [kJ mol ⁻¹]	-	-	5.42
n [-]	-	-	1.29

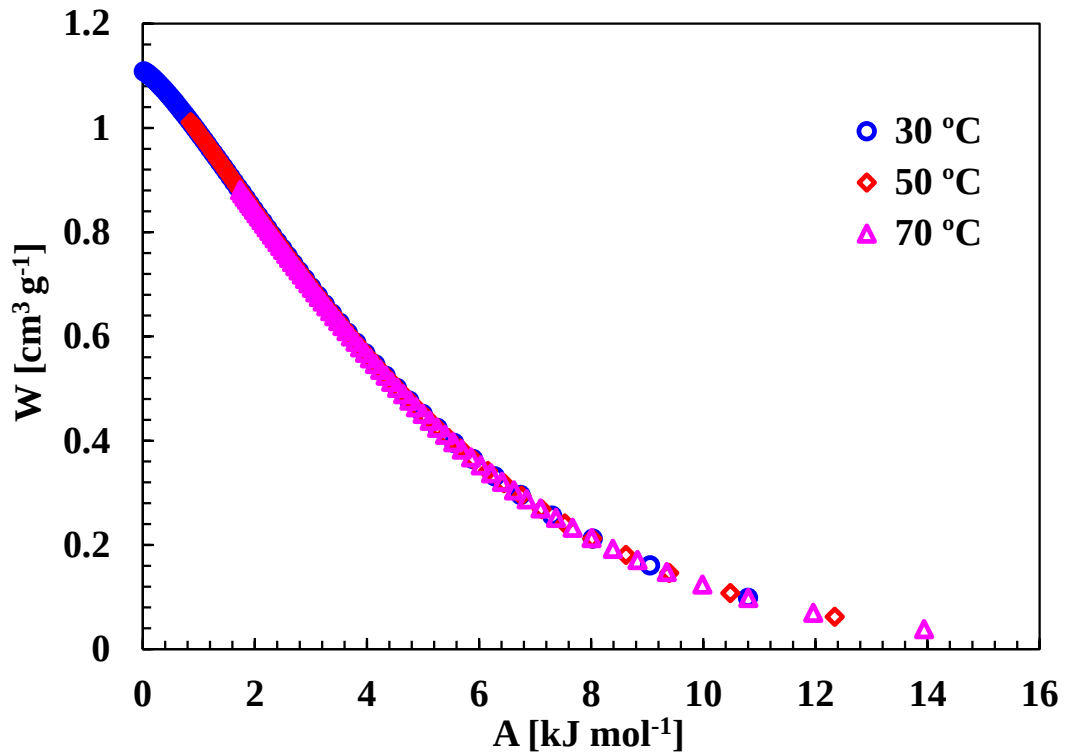


Fig. 5.13 Characteristic curve for the composite C/CO₂ pair using modified Dubinin-Astakhov (D-A) equation.

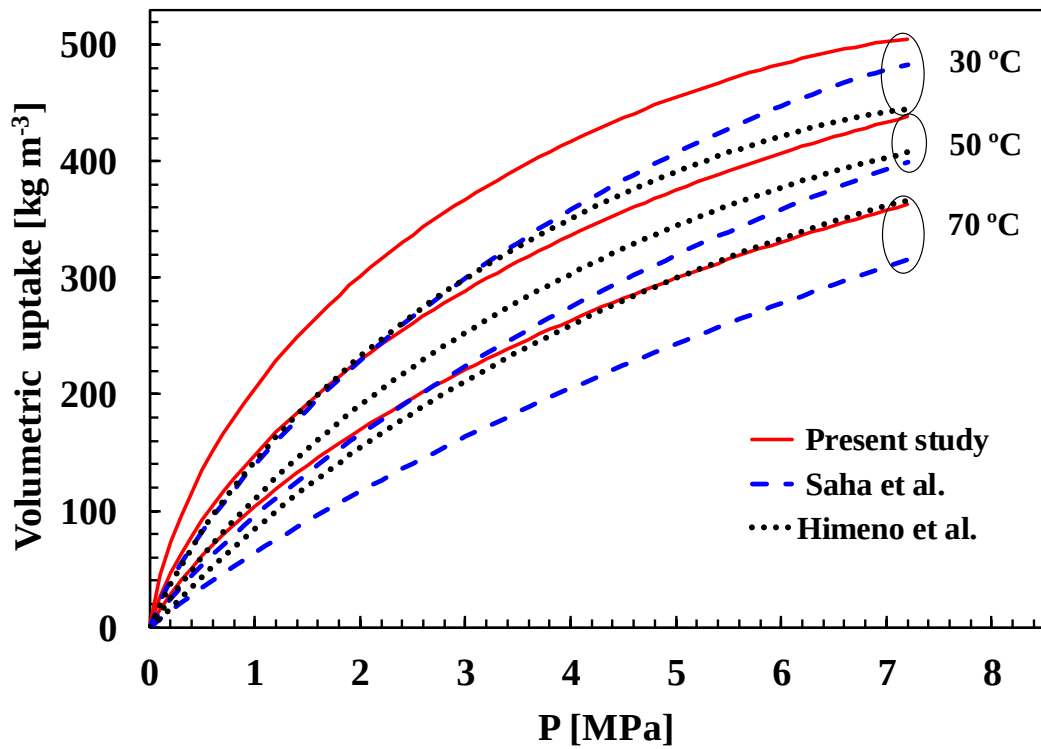


Fig. 5.14 Comparison of volumetric adsorption uptake of CO₂ among studied consolidated composite, Saha et al. [52] and Himeno et al. [36].

5.6.2 GNPs contained composites/CO₂ pairs

5.6.2.1 Adsorption isotherms

The characteristics of synthesized of GNPs contained composites were discussed in chapter 3. Among them, composite 1, 2, and 4 are selected for CO₂ adsorption. The details of experimental procedure were described in section 1.2 of this chapter. Figs 5.15 – 5.17 illustrate the equilibrium absolute absorption uptake of CO₂ onto composite 1, 2 and 4, respectively. The experimental data are fitted with Tóth and modified D-A isotherm model which are plotted on the same figures. As can be seen from Figs 5.15 – 5.17, there is a very good agreement between the experimental and predicted data from both isotherm models for all composites/CO₂ pairs. The root-mean-square deviation and all other estimated isotherm parameter are furnished in Table 5.5. It is found that composite 1 possess higher adsorption capacity of CO₂ compared to all other composites because it contains a higher amount of Maxsorb III and without thermal conductivity enhancer. In addition, C-grade GNPs contained composite 4 shows slightly higher adsorption uptake than that of H-grade contained composite 2 as can be seen from Table 5.5. Although both composites contain the same composition of additives materials, due to porous properties of C-grade GNPs contributed adsorption affinity towards the CO₂ gas molecules. It can be mentioned that composite 1 can adsorb CO₂ about 1.4331 cm³ g⁻¹ whilst 1.1880 cm³ g⁻¹ and 1.2181 cm³ g⁻¹ are for composite 2 and 4, respectively.

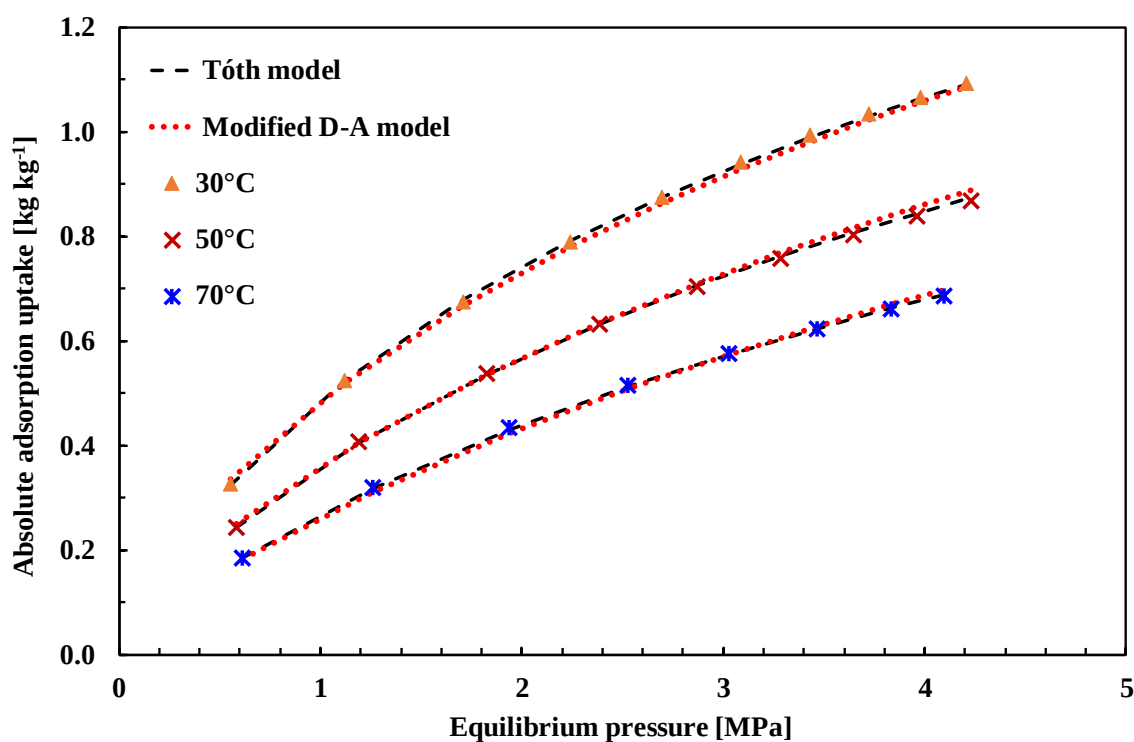


Fig. 5.15 Adsorption isotherms of the composite 1/CO₂ pair (data are fitted with Tóth and modified D-A model).

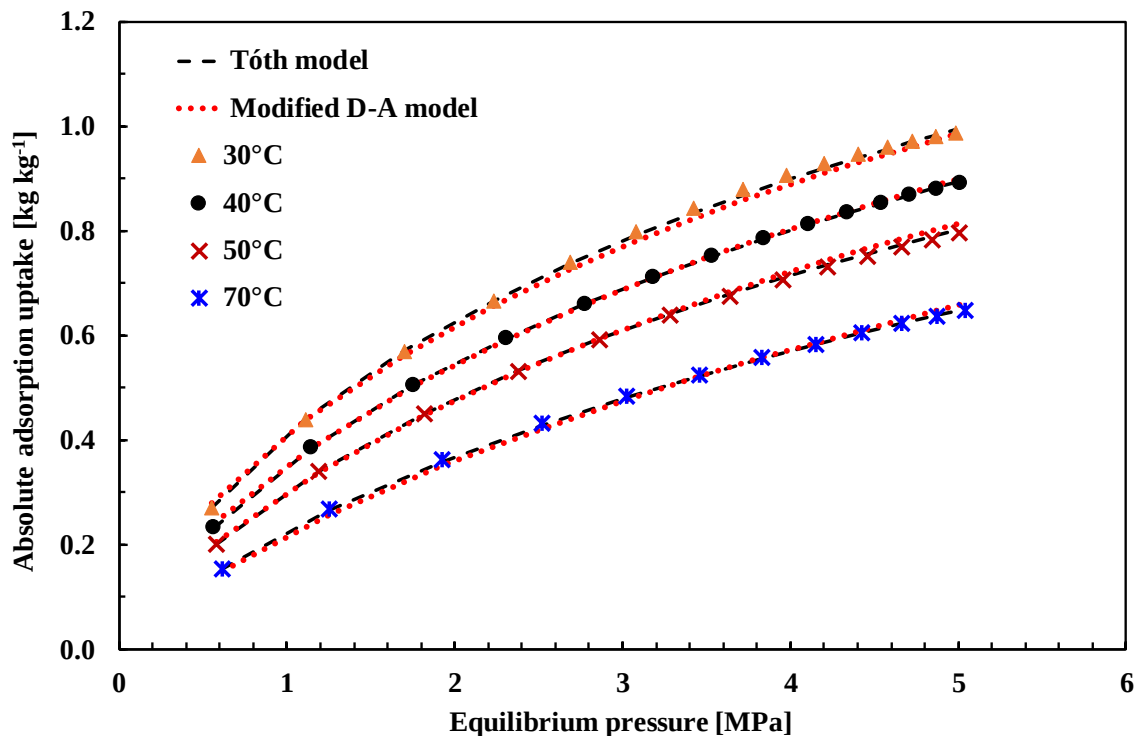


Fig. 5.16 Adsorption isotherms of the composite 2/CO₂ pair (data are fitted with Tóth and modified D-A model).

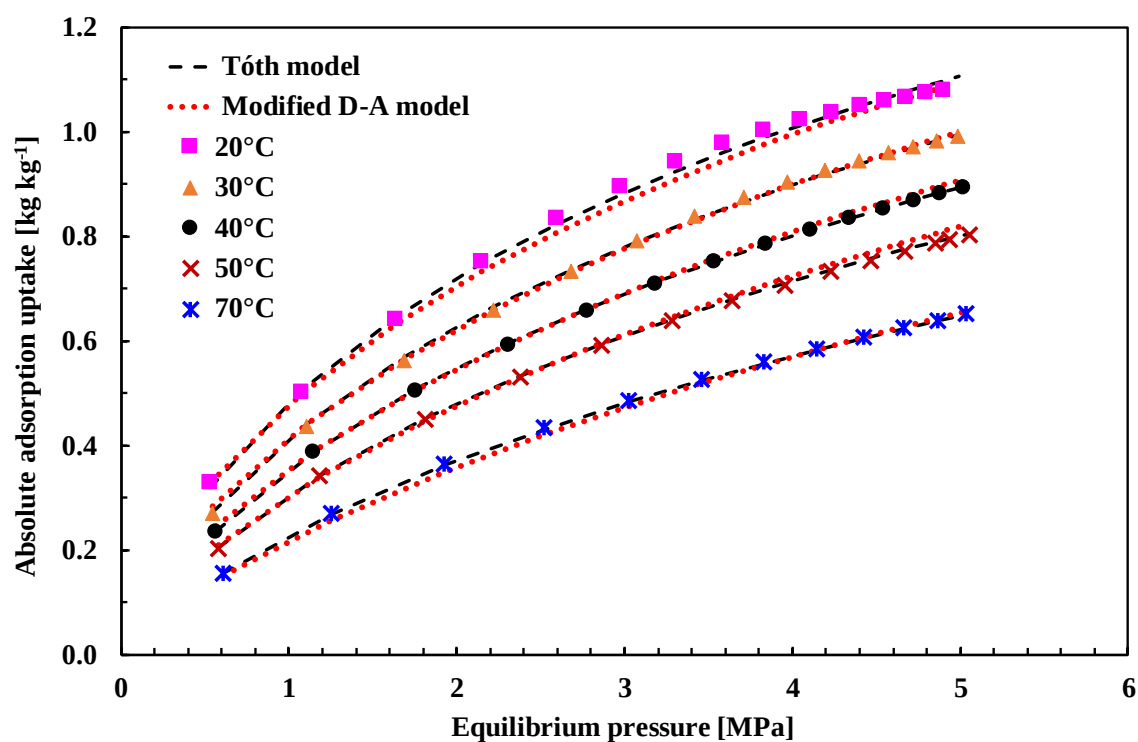


Fig. 5.17 Adsorption isotherms of the composite 4/CO₂ pair (data are fitted with Tóth and modified D-A model).

Table 5.5 Fitting parameters of the studied isotherm models for biomass-derived ACs/CO₂ pairs.

Model	Fitting parameters	composite 1	composite 2	composite 4
Modified D-A	q_0 [cm ³ g ⁻¹]	1.4331	1.1880	1.2181
	E [kJ mol ⁻¹]	4.885	4.956	4.891
	k [-]	3.906	4.073	4.221
	n [-]	1.183	1.211	1.176
	RMSD [%]	1.539	1.669	1.852
Tóth	W_0 [kg kg ⁻¹]	3.7020	2.9371	3.1050
	Q_{st} [J mol ⁻¹]	18373.76	1856.95	18564.92
	h [-]	0.518	0.540	0.515
	b_0 [MPa ⁻¹]	2.066×10^{-4}	1.959×10^{-4}	1.964×10^{-5}
	RMSD [%]	0.419	0.572	0.867

5.6.2.2 Adsorption kinetics

Normalized adsorption uptake as a function of time for composite 1, 2, and 4/CO₂ pairs along with Maxsorb III/CO₂ pair is shown in Fig. 5.18. There is no significant difference in time constant for reaching 63% of its equilibrium uptake among all the composites and Maxsorb III. Since CO₂ is higher pressure adsorbate gas. As a result, all samples reach their equilibrium value very quickly. However, absolute uptake rate of CO₂ onto all composites and Maxsorb III are different because of their adsorption capacity. The absolute uptake rate of composites/CO₂ pairs is less than Maxsorb III/CO₂ as shown in Fig. 5.19. It is also seen from Fig. 5.19 that same composition ratios composites show almost same absolute adsorption rate of CO₂ at a given time and pressure.

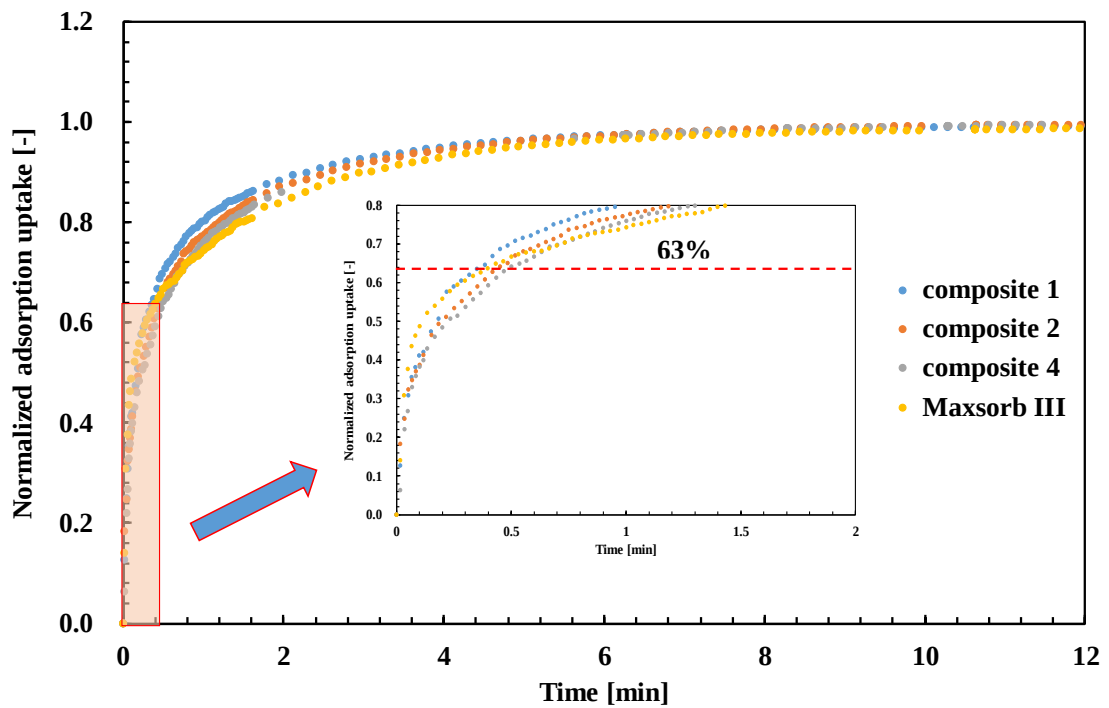


Fig. 5.18 Normalized adsorption uptake as a function of time for all composites/ CO_2 pairs along with Maxsorb III/ CO_2 pair at adsorption temperature 30°C and evaporator pressure about 560 kPa.

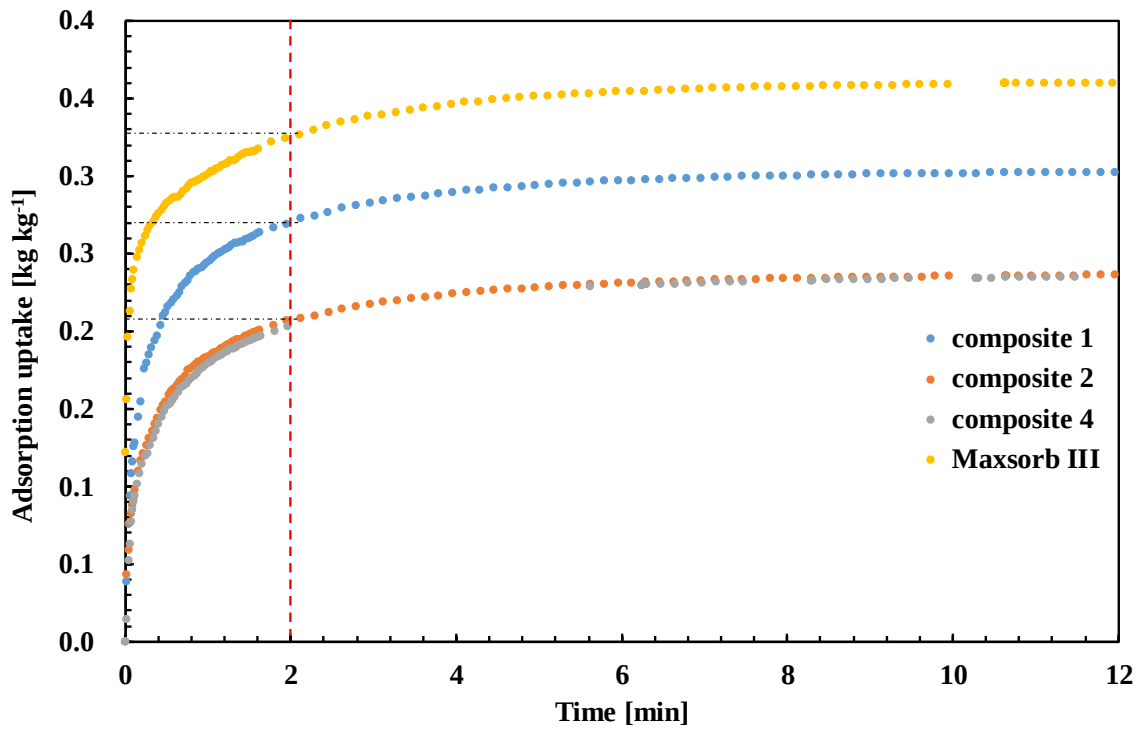


Fig. 5.19 Instantaneous absolute uptake of all composites/ CO_2 pairs along with Maxsorb III/ CO_2 pair at same condition presented in Fig. 5.18.

5.7 Conclusions

Biomass-derived ACs: Adsorption of CO₂ onto biomass-derived four AC samples has been measured at adsorption temperatures 25 to 70°C with pressure up to 7 MPa. For all pairs, it is found that Tóth and modified D-A model fit well with the experimental data within $\pm 5\%$ root-mean-square deviation (RMSD). The maximum absolute uptake is found about 2.6 cm³ g⁻¹ for WC500/pair followed by 2.4 cm³ g⁻¹, 2.3 cm³ g⁻¹, and 2.1 cm³ g⁻¹ for MC500, WC600, and MC600/CO₂ pair, respectively. However, Maxsorb III/CO₂ pair shows only the absolute uptake 1.5 cm³ g⁻¹. It should be highlighted that biomass-derived all four ACs show very high adsorption uptake which is about 40% to 73% enhanced uptake compared to Maxsorb III/CO₂ pair. This reason behind this that all synthesized biomass-derived ACs possess very high pore volume. Furthermore, isosteric heat of adsorption (Q_{st}) is also lower for biomass-derived ACs that is good for cooling applications. It is found that all biomass-derived ACs shows a high percentage of ΔW improvement compared to Maxsorb III and Norit RB3. The highest improvement is found 176% and 506% compared to Maxsorb III and Norit RB3, respectively. There is no significant difference in time constant for reaching 63% of its equilibrium adsorption uptake among the WPT-AC and M-AC samples. Since CO₂ is higher pressure adsorbate gas, as a result, all samples reach their equilibrium value very rapidly. The absolute adsorption rate of CO₂ onto biomass-derived ACs is higher than Maxsorb III and among them, WPT-AC (C600) is the highest followed by WPT-AC(C500), M-AC (C500) and M-AC (C600) at a given time. Therefore, biomass-derived ACs are very promising for CO₂ based adsorption systems.

EG contained AC composites: Adsorption of carbon dioxide onto a consolidated composite adsorbent has been experimentally investigated at three different adsorption temperatures namely, 30, 50, and 70°C and pressures ranging from 0 to 7 MPa. The measured adsorption isotherms data have been successfully fitted with the three isotherm models namely, Langmuir, Tóth, and modified Dubinin-Astakhov (D-A) equation. The volumetric adsorption capacity of CO₂ onto the consolidated composite is compared with that of Maxsorb III/CO₂ pair. The isosteric heat of adsorption of studied adsorbent/refrigerant pair has been predicted from the isotherm data, and the average value of Q_{st} is found to be 22.5 kJ mol⁻¹.

GNPs contained AC composites : The CO₂ adsorption characteristics onto GNPs contained composite 1, 2, and 4 are measured thermogravimetric method at adsorption

temperatures 30-70°C and pressure up to 5 MPa. The experimental data are fitted with Tóth and modified D-A isotherm model and found good agreement between the experimental and predicted data from both isotherm models for all composites/CO₂ pairs. It is found that composite 1 possess higher adsorption capacity of CO₂ compared to all other composites because it contains a higher amount of Maxsorb III. In addition, C-grade GNPs contained composite 4 shows slightly higher adsorption uptake than that of H-grade contained composite 2, although both composites contain the same composition of additives materials. This phenomenon might be attributed to the higher porous properties of C-grade GNPs than H-grade. It is noticed that composite 1 can adsorb CO₂ about 1.4331 cm³ g⁻¹ whilst 1.1880 cm³ g⁻¹ and 1.2181 cm³ g⁻¹ are for composite 2 and 4, respectively. The adsorption uptake variation with time shows there is no significant time difference among all the composites/CO₂ pairs to reach of its any equilibrium uptake value. However, absolute uptake rate of CO₂ onto all composites and Maxsorb III are different because of their adsorption capacity and found Maxsorb III/CO₂ pair is higher than composites/CO₂ pairs. Conversely, all composites/CO₂ pairs show almost same absolute adsorption rate. With the advent of the technological improvement for heat exchangers, composite adsorbent materials can be packed inside the adsorber/desorber heat exchanger, which will lead to notable performance improvement in adsorption cooling and heat pump systems.

Chapter 6

Thermodynamic analysis of an adsorption cooling cycle

In this chapter, a thermodynamic analysis of an equilibrium adsorption cooling cycle using; i) biomass-derived ACs/ethanol and CO₂; ii) composites/ethanol and CO₂ pairs and along with Maxsorb III/ethanol and CO₂ pairs have been presented. The relationship between equilibrium pressure, adsorption capacity, and adsorption temperature are determined. The performance of typical adsorption cooling cycle has been discussed at three different evaporator temperatures, namely 5, 10 and 15°C along with a coolant temperature of 30°C and heat source temperatures ranging from 45 to 100°C by considering a time-independent thermodynamic model.

6.1 Introduction

The research on adsorption cooling and heat pump system got momentum after observing the worldwide energy crisis in the 1970s together with the imposition of international protocols which limits the production and utilization of CFCs, HCFCs as a refrigerant in the 1980s [157–159]. AHP is found a safe alternative to the conventional system because of the following features: i) it can be driven by low-grade waste heat or solar heat, typically below 100°C ii) it can use natural fluid as refrigerant, iii) it uses minimum movable parts, iv) no electricity usage other than the heat transfer fluid pumps and electromagnetic valves [11,160–162]. Therefore, AHP contributes to the conservation of electrical energy and environmental protection of using low-grade industrial waste heat or solar heat and refrigerant having zero ODP and zero GWP. Notable researchers extensively studied several adsorbent/refrigerant pairs for application to AHP systems, for instances; silica gel-water [9,11,103,151,161,163–165]; zeolite-water/-ethanol [152,166–170]; activated carbon (AC)-ethanol/-methanol/-R32/-R134a/-R410A/-R404A/-R152a/-CO₂ [33,34,52,57,80,90,97,102,105,135,149,150,171–178]; MOF-ethanol/-water/-CO₂ [55,179–181]; ACF-ethanol/-methanol/-R32/-CO₂ [52–54,76,182] and composite-

ethanol/-methanol/-CO₂ pair [69,89,117]. Among these pairs, activated carbon and carbon based composites/ethanol and the CO₂ pair are considered very much potential for AHP application because of AC possesses very high surface area and pore volume, which are prerequisite for a high amount of gas molecules adsorption. Furthermore, ethanol and CO₂ are environment-friendly refrigerants. It is also proven by numerous researchers [14,15,18,101,102,149,183,184] that AC powder has promising adsorption characteristics with the refrigerant of ethanol and CO₂.

In the present chapter, the performance of time-independent ethanol and CO₂ based equilibrium adsorption heat pump cycle using the biomass-derived AC and composites has been investigated and compared with literature. The analysis has been done at three different evaporator temperatures namely 5, 10 and 15°C along with an adsorption temperature at 30°C and desorption temperatures ranging from 45 to 90°C for both refrigerants based equilibrium adsorption cycle.

6.2 Thermodynamic cycle

The schematic diagram of adsorption cooling system and the thermodynamic processes of a basic adsorption cycle are shown in Fig. 6.1 and Fig. 6.2, respectively. It consists of an evaporator, a condenser, an adsorber/desorber, and a throttling valve or a bending capillary tube, which is used to connect the condenser and the evaporator. As can be seen from Fig. 6.2, the ideal cycle consists of four steps, which are pre-heating, desorption process, pre-cooling, and adsorption process. In the first step, the adsorber is disconnected from both the evaporator and the condenser. It is then heated by external heat source at constant refrigerant concentration, which results in the temperature increase of refrigerant from $T_{e,a}$ to $T_{s,d}$. The adsorber pressure increases from the evaporating pressure up to the condensing pressure. In the second step, adsorber is connected to the condenser and the heat added from external source continues in this process. The refrigerant vapor is desorbed at constant pressure, P_c , while the temperature increases until it reaches the desorption temperature, $T_{e,d}$. The desorbed refrigerant vapour is liquefied in the condenser and the condensing heat is removed by coolant temperature T_c that flows inside the condenser heat transfer tubes. In the pre-cooling process, the adsorber is isolated from both the evaporator and the condenser. It is then cooled down at a constant refrigerant concentration from $T_{e,d}$ to $T_{s,a}$ by the coolant. The pressure of the adsorber decreases

from condenser pressure down to the evaporator pressure. In the last step, the adsorber is connected to the evaporator and adsorbs the refrigerant vapour from the evaporator. During the adsorption process, the adsorber is cooled from $T_{s,a}$ to $T_{e,a}$. Adsorption heat is removed by coolant that flows inside the adsorber.

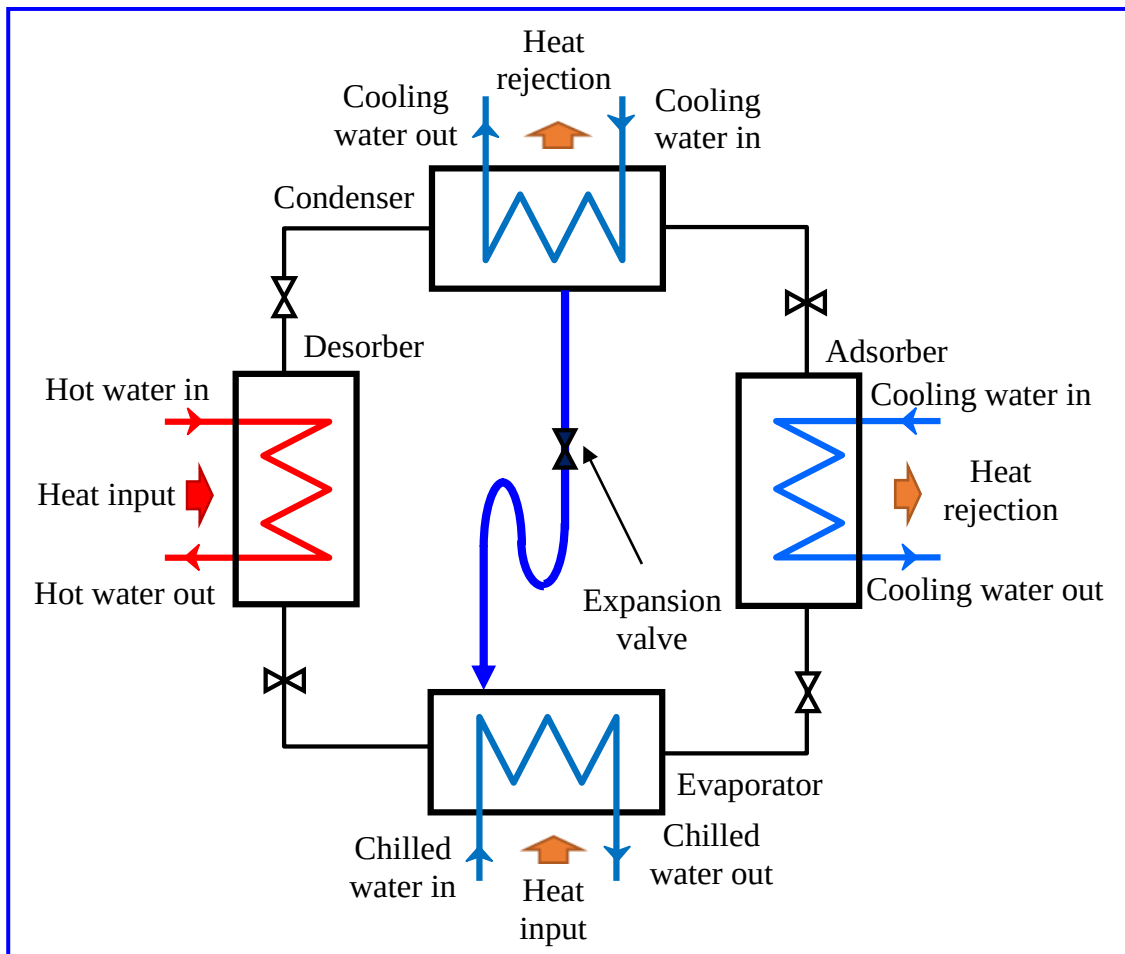


Fig. 6.1 Schematic diagram of basic adsorption cooling system.

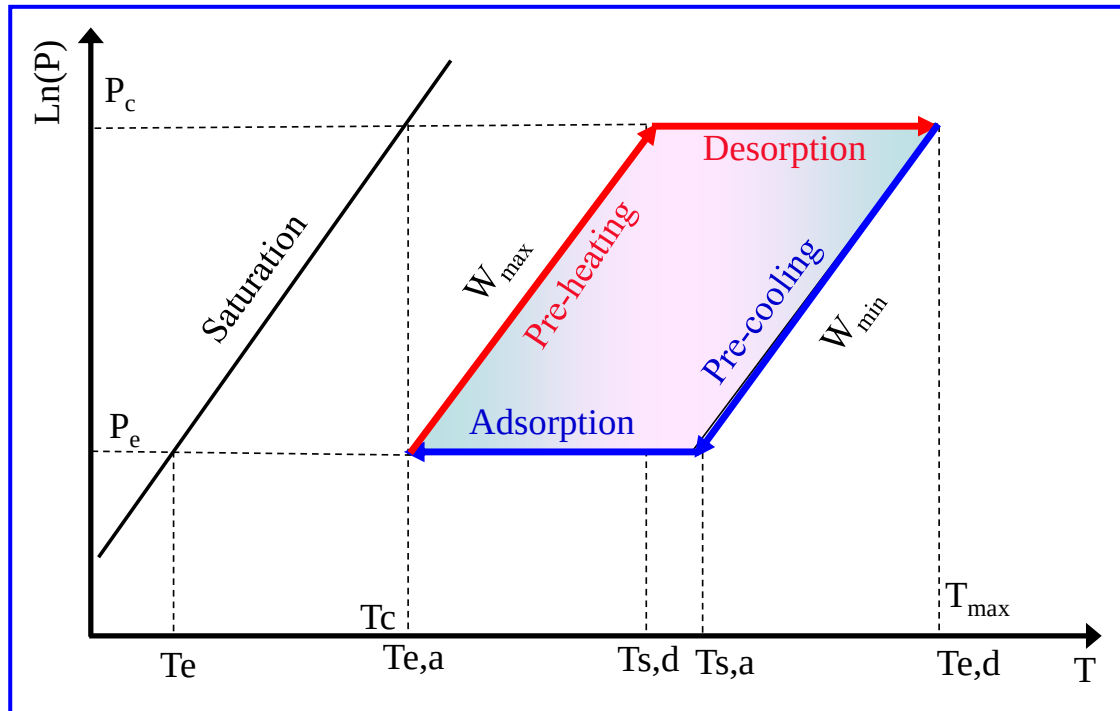


Fig. 6.2 Thermodynamic process of the basic adsorption cooling cycle.

The pressure–temperature–concentration (P-T-W) diagram is used to analysis the performance of an ideal adsorption cooling cycle. It shows the thermodynamic relation between the equilibrium pressure, adsorbent temperature and adsorption capacity at equilibrium conditions. The D-A equation has been used to draw the P-T-W diagram of composite A/ethanol pair and composite C/ethanol pair, which are shown in Fig. 6.3 (a) and (b), respectively. This drawing demonstrates a representation of pressure–temperature–concentration plot with adsorption cooling cycle for calculation of SCE (specific cooling effect) and COP (coefficient of performance).

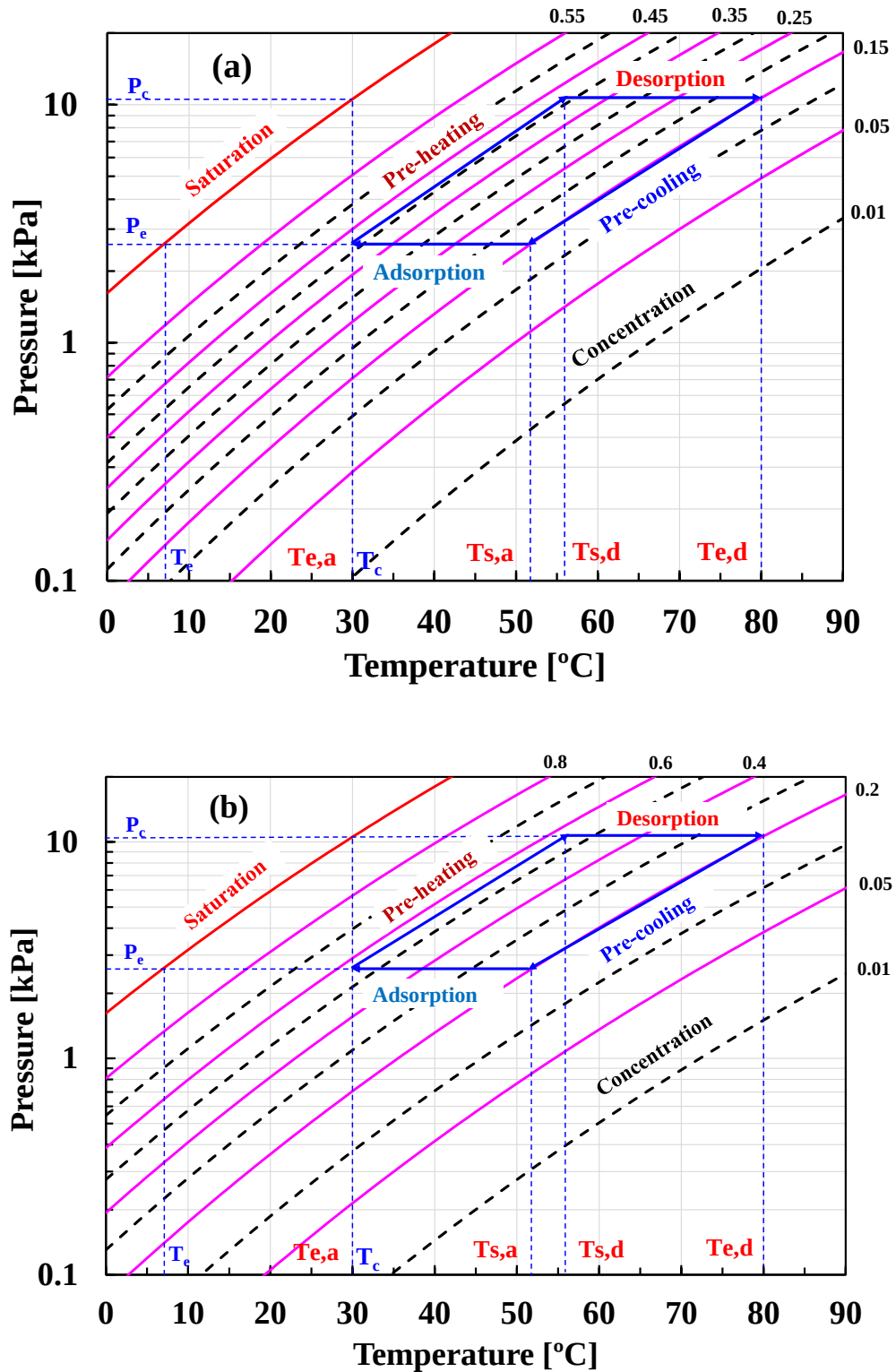


Fig. 6.3 A representative illustration of P-T-W diagram with adsorption cycle of (a) composite A (50% Maxsorb III + 40% EG + 10% PVA)/ethanol pair, and (b) composite C (50% Maxsorb III + 40% EG + 10% PVA)/ethanol pair.

The model described here is a thermodynamical equilibrium model. This means all the thermal contributions are calculated based on heat and mass balance provided by the (P-T-W) diagrams.

Specific cooling effect (SCE) can be defined as the following equation:

$$SCE = (W_{\max} - W_{\min}) \left[h_{fg}(T_e) - \int_{T_e}^{T_c} dh_f \right] \quad (6.1)$$

The coefficient of performance (COP) can be written as:

$$COP = \frac{SCE}{Q_{\text{sens}} + Q_{\text{latent}}} \quad (6.2)$$

Where,

$$Q_{\text{sens}} = \int_{T_{e,a}}^{T_{e,d}} C_{p_{ad}} dT + W_{\max} \int_{T_{e,a}}^{T_{s,d}} C_{p_{ref}} dT + \int_{T_{s,d}}^{T_{e,d}} W C_{p_{ref}} dT \quad (6.3)$$

$$\text{And } Q_{\text{latent}} = Q_{st} \int_{W_{\max}}^{W_{\min}} dW \quad (6.4)$$

In the equation (6.3), the first term defines the sensible heat added to the adsorbent consequently its temperature increases from $T_{e,a}$ to $T_{e,d}$ whilst the second and third terms are represented sensible heat added to the refrigerant during pre-heating and the desorption process, respectively. The specific heat capacity of adsorbent ($C_{p_{ad}}$) is calculated according to the references [46,74] and has been taken the average for the range of temperature utilized. Q_{st} is the heat of adsorption in the equation (6.4). The Clausius–Clapeyron equation (6.5) is used to compute the average value of the heat of adsorption.

$$\frac{-Q_{st(CC)}M}{R} = \frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \quad (6.5)$$

6.3 Effect of operating temperature on SCE and COP

In this study, two environmental friendly refrigerants (ethanol and CO₂) and has been employed for calculating SCE and COP with the variation of operating temperatures. The following sections discuss the ethanol and CO₂ based equilibrium adsorption cooling cycle. A series of biomass-derived ACs and composites adsorbents are selected for the calculation of SCE and COP for both refrigerants. Adsorbents properties and all other characteristics parameter have already been discussed in the previous chapter 3, 4 and 5.

6.3.1 Ethanol as a refrigerant

6.3.1.1 Biomass-derived ACs

The pressure–temperature–concentration (P-T-W) diagram is used to analysis the performance of an ideal adsorption cooling cycle. It shows the thermodynamic relation between the equilibrium pressure, adsorbent temperature and adsorption capacity at equilibrium conditions. The D-A equation has been used to draw the P-T-W diagram for all studied AC adsorbents. Fig. 6.4 and Fig. 6.5 show the effect of desorption temperature on the SCE of WPT-AC (WC600A900K6)/ethanol and M-AC (MC600A900K6)/ethanol pairs, respectively, at three different evaporator temperatures, namely 5, 10, and 15°C with adsorption temperature at 30°C. It is observed that higher evaporator temperature gives higher cooling effect because of higher evaporation rate and uptake. It is seen that the SCE increases linearly with the increases of desorption temperature for both samples. This is due to the increases of concentration difference with the increases of desorption temperature at constant adsorption and evaporator temperatures. It is found that WPT-AC/ethanol adsorption cycle can achieve SCE about 1067 kJ kg⁻¹ at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC/ethanol pair provides about 1036 kJ kg⁻¹. In the previous chapter mentioned that porous properties and adsorption characteristics of biomass-derived ACs are superior to Maxsorb III AC. Here, this study also compares the SCE among them. Fig. 6.6 shows the comparison of specific cooling effect (SCE) among biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs at evaporator temperature 15°C with the function of desorption temperature. It is found that Maxsorb III/ethanol adsorption cycle can achieve SCE about 782 kJ kg⁻¹ at evaporation and heat source temperature are 15°C and 100°C, respectively. It can be seen that WPT-AC/ethanol and M-AC/ethanol both pairs provide very high SCE compared to

Maxsorb III/ethanol in the studied desorption temperatures. It is highlighted that WPT-AC/ethanol adsorption cycle shows 36% higher SCE whilst M-AC/ethanol pair gives about 32% higher SCE compared to Maxsorb III/ethanol at evaporation temperature 15°C along heat source temperature 100°C.

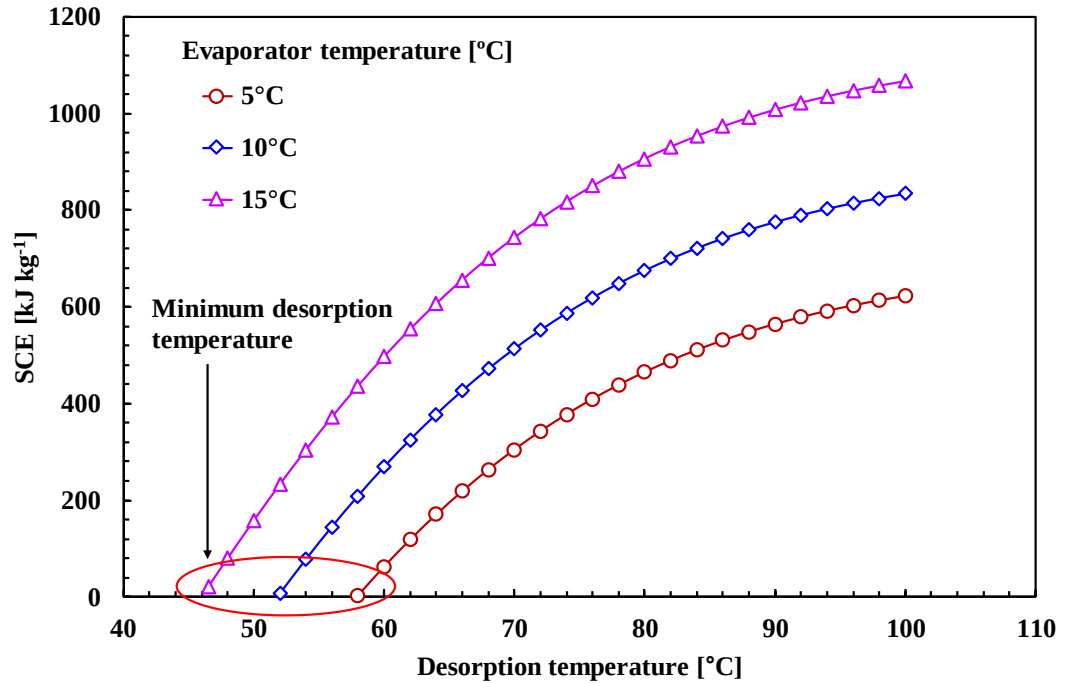


Fig. 6.4 Specific cooling effect (SCE) of WPT-AC (WC600A900K6)/ethanol pair with a function of desorption temperature.

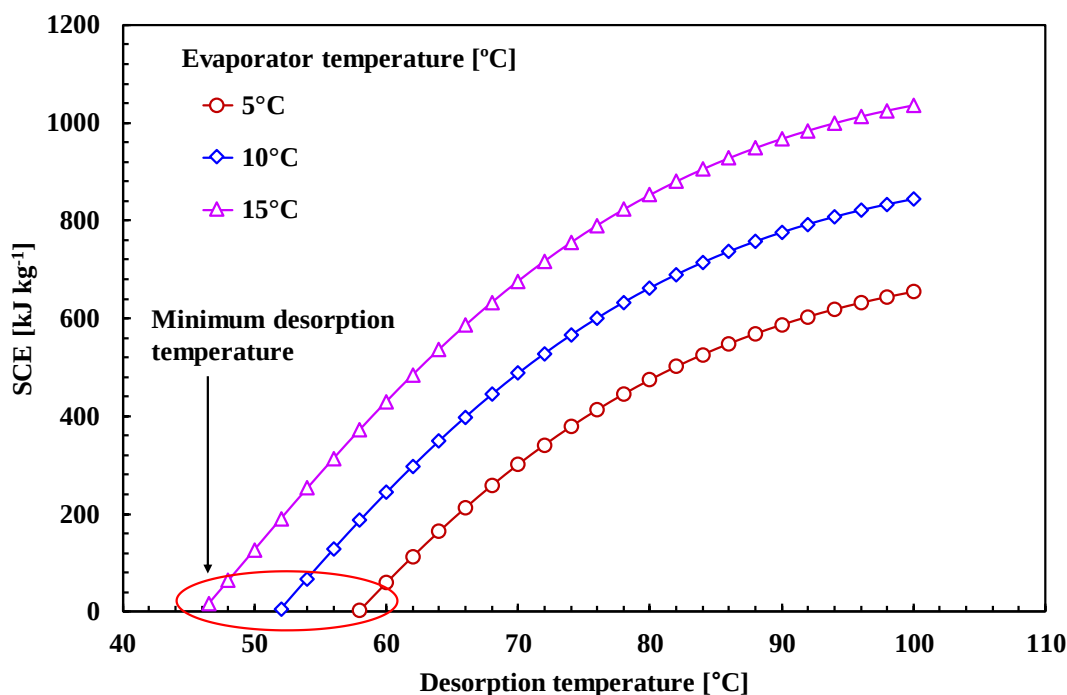


Fig. 6.5 Specific cooling effect (SCE) of M-AC (MC600A900K6)/ethanol pair with a function of desorption temperature.

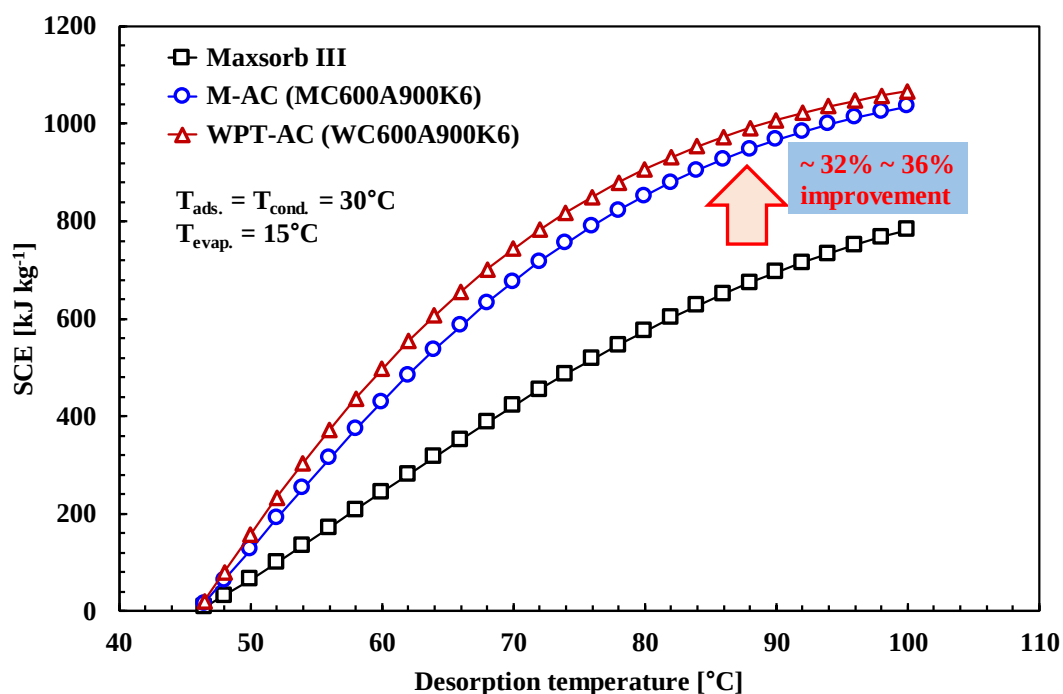


Fig. 6.6 Comparison of specific cooling effect (SCE) among biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.

A correlation was proposed by Saha et al. [185] to estimate the minimum desorption temperature for adsorption cooling cycle operation which is given by equation (6.6). The minimum required desorption temperature changes with the change of the evaporation temperature.

$$T_{\min_des} = \frac{T_c^2}{T_e} \quad (6.6)$$

Where $T_{\min_des}$, T_e , and T_c are minimum desorption, evaporation, and adsorption or condenser temperatures, respectively. At evaporation 5, 10 and 15°C, the corresponding minimum desorption temperature are 57.2, 51.4 and 45.8°C.

As can be seen in Fig. 6.4 and Fig. 6.5, the calculated SCE values are near zero corresponding to minimum desorption temperatures of an ideal cycle, which is a decent agreement between SCE and minimum desorption temperatures. The calculated minimum desorption temperature from ideal cycle analysis is well matched with the value obtained from the equation (6.6) for studied three evaporator temperatures. It is observed that calculated minimum desorption temperature from ideal cycle analysis is less than 1°C higher than that of calculated using equation (6.6). Therefore, it can be said that minimum desorption temperature of biomass-derived ACs/ethanol pairs are well matched with the theoretical equation derived from D-A equation.

Fig. 6.7 and Fig. 6.8 show the effect of desorption temperature on COP of both pairs, respectively. It can be seen that the COP increases sharply only when the desorption temperature is below 65°C. After that, the increase in COP is marginal even though the SCE increases. This happens due to the requirement of heat input becomes significantly large when the temperature difference between heat source and the heat sink is relatively high. The maximum COP of WPT-AC/ethanol and M-AC/ethanol based cooling systems are found to be 0.75 and 0.74, respectively. However, study shows that there is no significant COP difference among the biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs, as can be seen from Fig. 6.9.

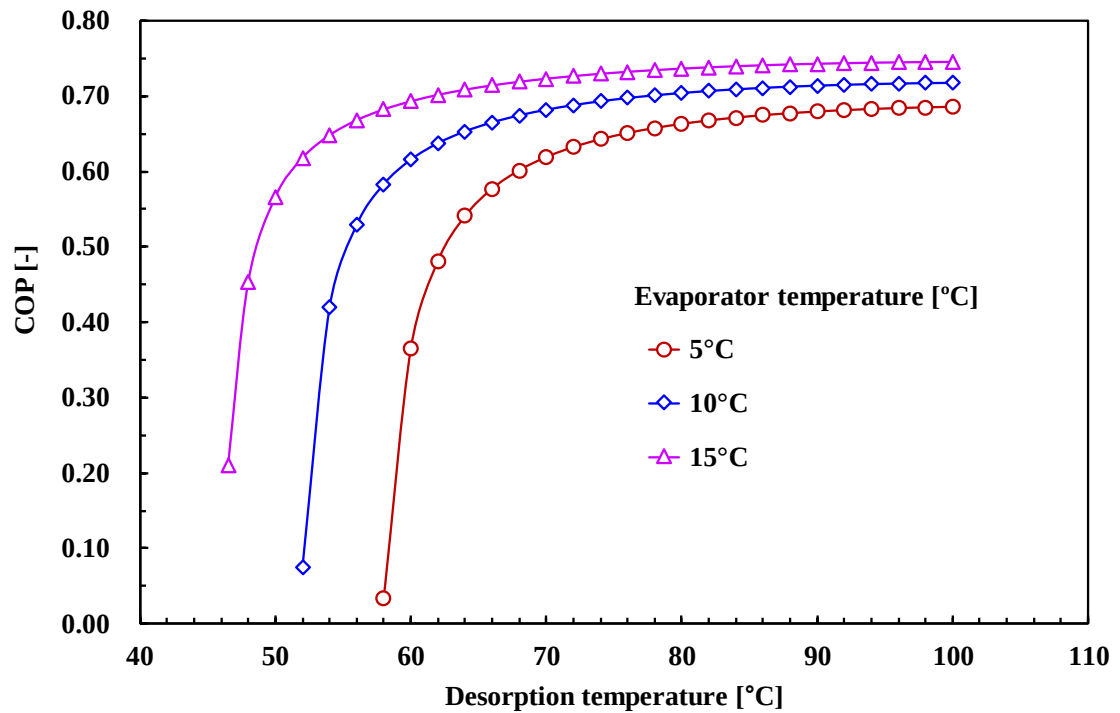


Fig. 6.7 COP of WPT-AC (WC600A900K6)/ethanol with a function of desorption temperature.

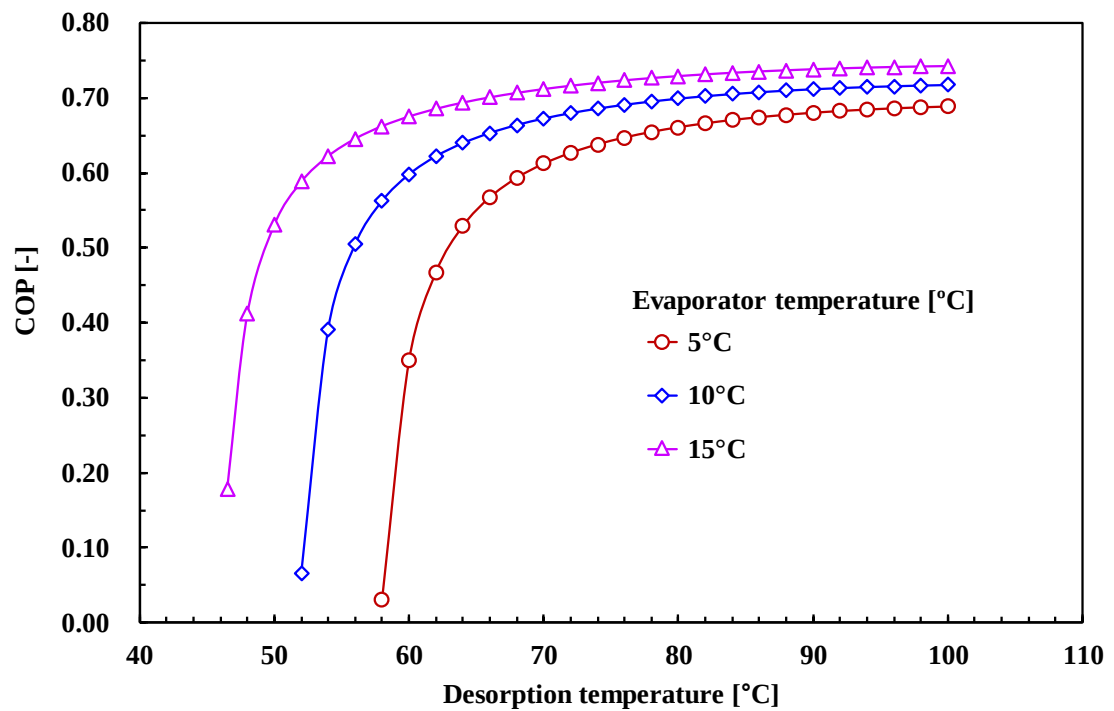


Fig. 6.8 COP of M-AC (MC600A900K6)/ethanol with a function of desorption temperature.

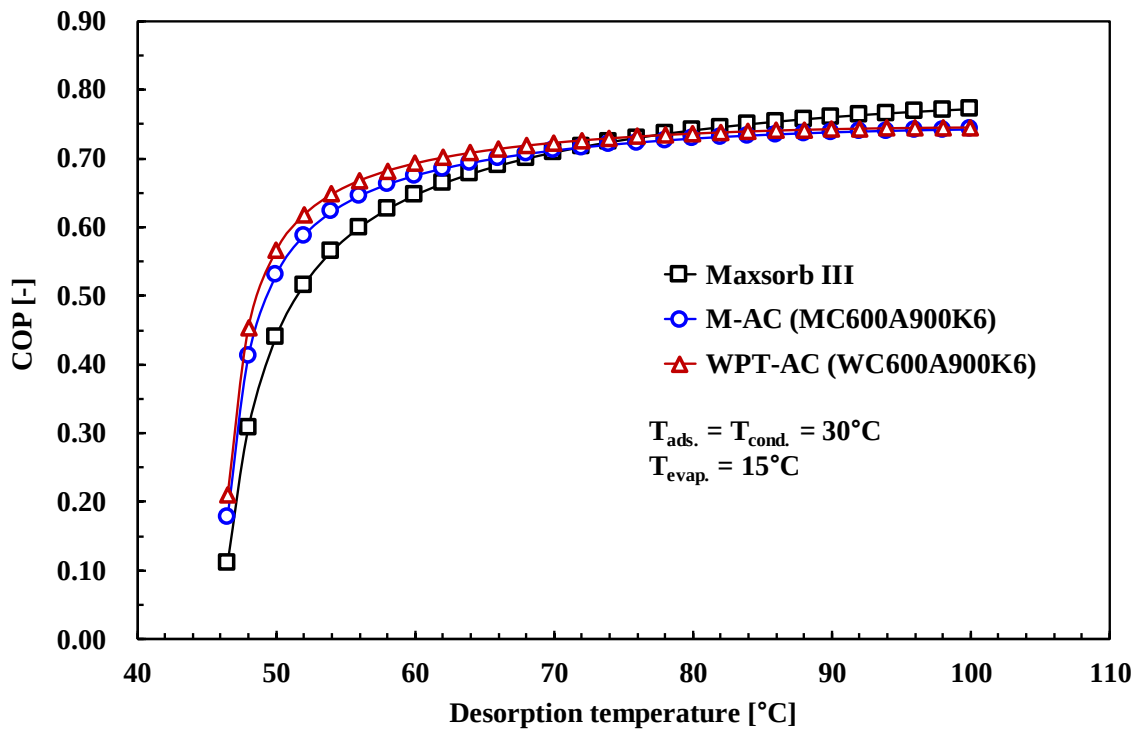


Fig. 6.9 Comparison of COP among biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.

6.3.1.2 Composite adsorbents

In this section, EG contained composites (composite A and composite C), Maxsorb III + PVA, GNPs contained composites (composite 2 to 3), and Maxsorb III + PIL composites/ethanol pairs are employed for calculating the SCE and COP. The porous properties and adsorption characteristics of ethanol have been discussed in chapter 3 and 4. Fig. 6.10 represents the SCE of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair at adsorption temperature 30°C along with three different evaporation temperature, namely 5, 10, and 15°C. Similar phenomena are also observed here as discussed in the previous section 6.3.1.1. It is found this studied pair provides 762 kJ kg⁻¹ cooling effect at adsorption, evaporation, and desorption temperature 30, 15 and 100°C, respectively. It is important to mention that similar phenomena are also observed for all other studied composites/ethanol pairs. All composites/ethanol pairs also obey the equation (6.6) for obtaining minimum desorption temperature as shown in Fig. 6.10. The comparison of SCE among all studied composites/ethanol pairs is shown in Fig. 6.11. It can be seen that polymerized IL contained composite/ethanol pair shows higher SCE than

any other composites and followed by composite 1, composite C, composite 4, composite 2, composite A and composite 3. Except for PIL composite and composite 1, all other composites follow the percentage of parent adsorbent AC (Maxsorb III). For instances, SCE of 70 wt% Maxsorb III contained composites falls together and 50 wt% Maxsorb III contained composites also falls together. However, 90 wt % Maxsorb III contained does not fall together which implies that PIL as binder contained composite shows high SCE which means adsorption uptake and effective uptake is higher than any other composites.

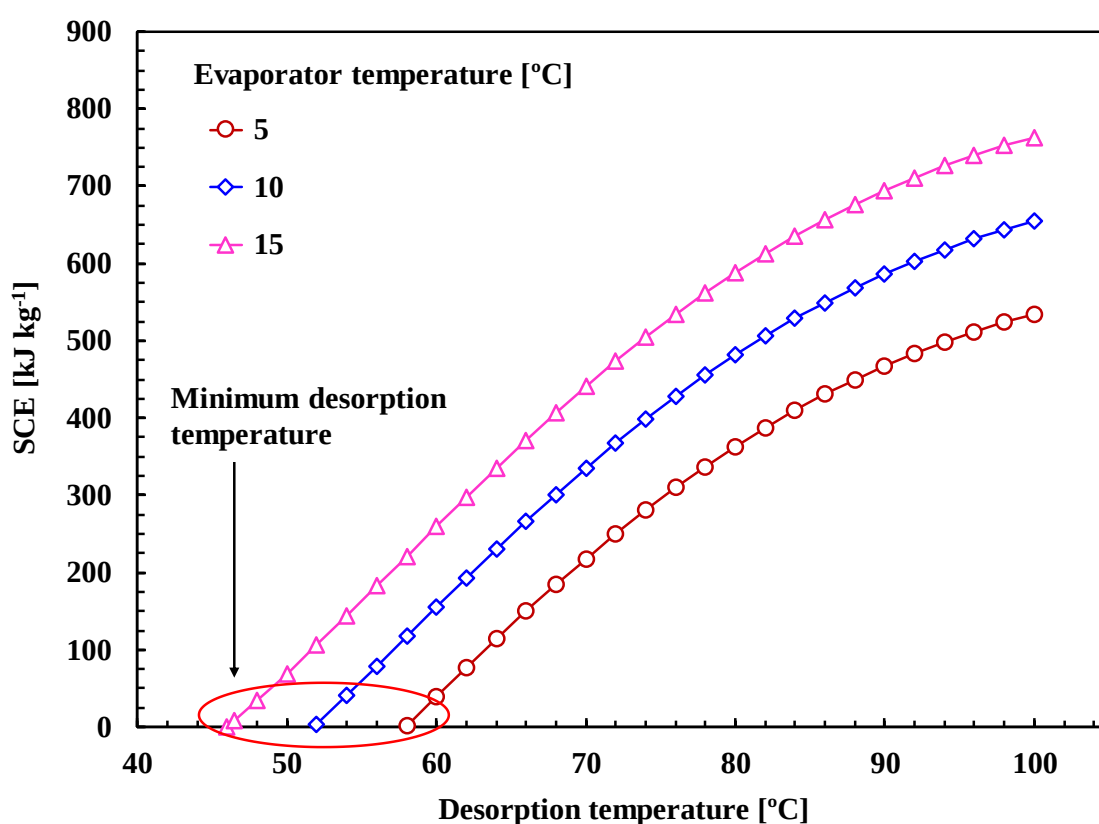


Fig. 6.10 A representative illustration of SCE of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair with a function of desorption temperature.

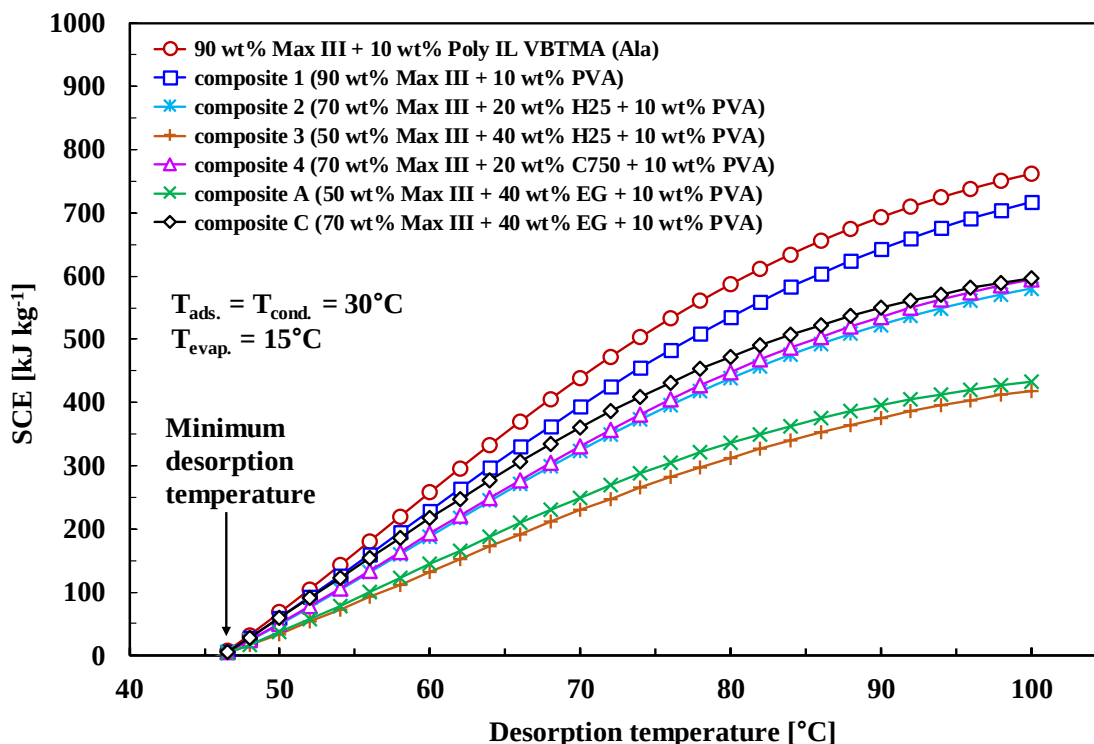


Fig. 6.11 Comparison of specific cooling effect (SCE) among all studied composites/ethanol pairs at evaporator temperature 15°C with a function of desorption temperature.

Fig. 6.12 shows the effect of desorption temperature on COP of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair. A similar characteristic is also observed here as discussed in case of ACs/ethanol pairs. The similar phenomenon is also observed for all other composites/ethanol. The maximum COP for PIL composite/ethanol pair is also found 0.8. However, study shows that there is marginal COP difference among all composites, as can be seen from Fig. 6.13. It is seen the maximum COP varies from 0.72 to 0.8 after the desorption temperature of 80°C.

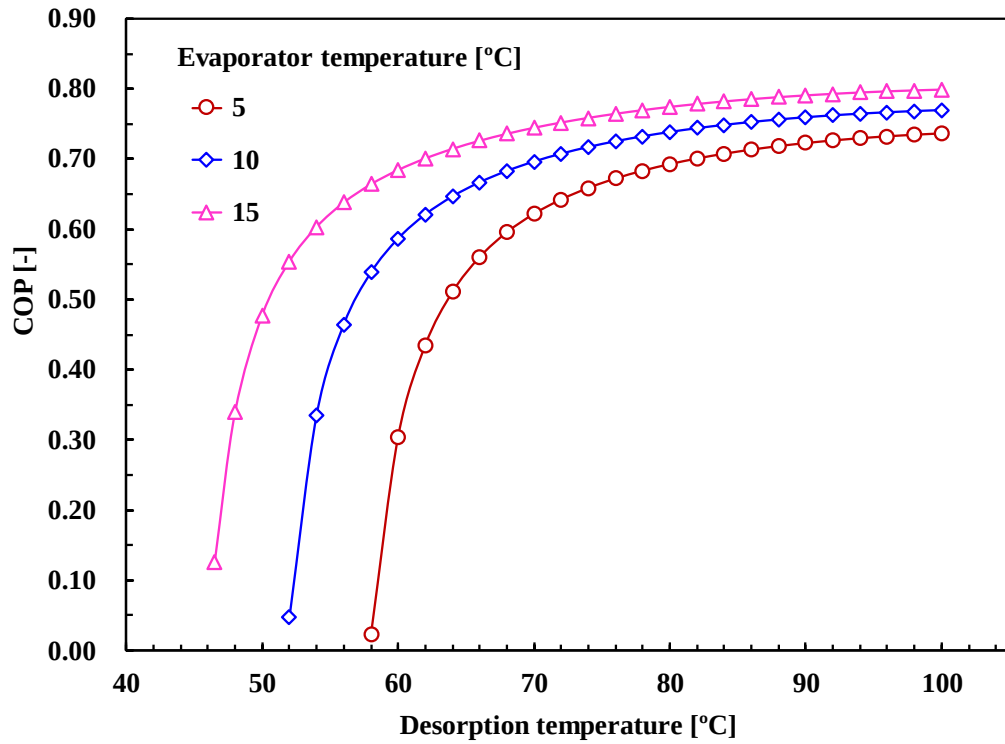


Fig. 6.12 A representative illustration of COP of Maxsorb III (90 wt%) + Poly IL VBTMA (Ala) (10 wt%)/ethanol pair with the function of desorption temperature.

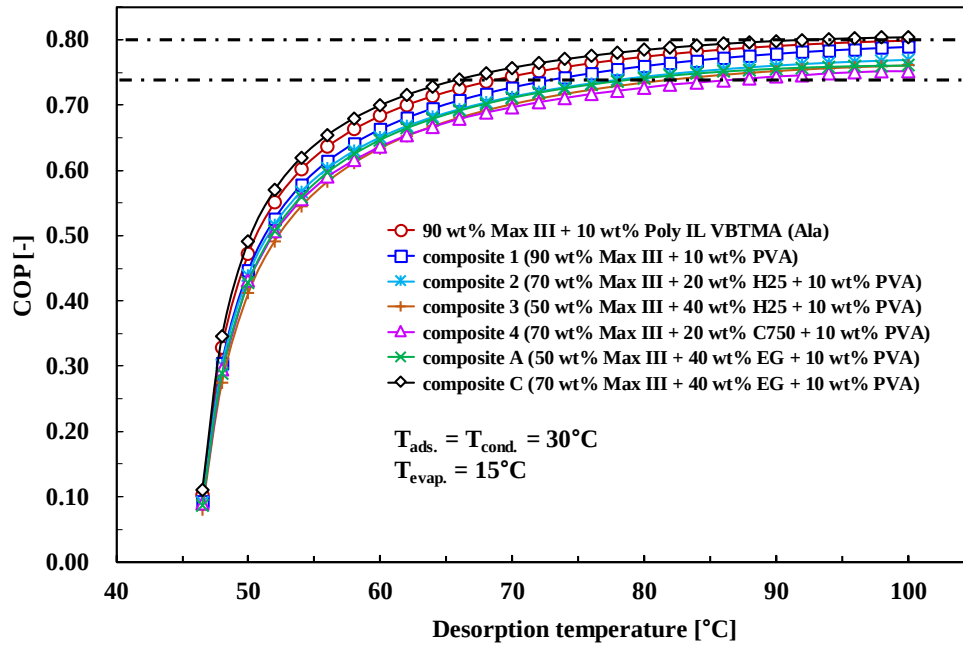


Fig. 6.13 Comparison of COP among all studied composites/ethanol pairs at evaporator temperature 15°C and adsorption temperature 30°C with the function of desorption temperature.

6.3.2 CO_2 as a refrigerant

6.3.2.1 Biomass-derived ACs

A similar analysis is also done for biomass-derived ACs/ CO_2 pair. Results of SCE show the similar trend line as like ACs/ethanol pair. However, SCE values are different because of refrigerant is different as can be seen from Fig. 6.14 and Fig. 6.15. It is found that WPT-AC (C500)/ CO_2 adsorption cycle can achieve SCE about 119 kJ kg^{-1} at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC (C500)/ethanol pair provides about 115 kJ kg^{-1} . It is noticed that minimum desorption temperatures for three evaporator temperatures are entirely different from calculated using equation (6.6). The values are 2 to 4°C higher than that of calculated from theoretical equation (6.6). However, in case of ACs/ethanol pair, it was just 1°C higher than that of theoretical value. The calculated minimum desorption temperature for WPT-AC (C500)/ CO_2 and M-AC (C500)/ CO_2 are marked in Fig. 6.14 and Fig. 6.15, respectively. Therefore, for biomass-derived ACs/ CO_2 pairs equation (6.6) will not be very accurate.

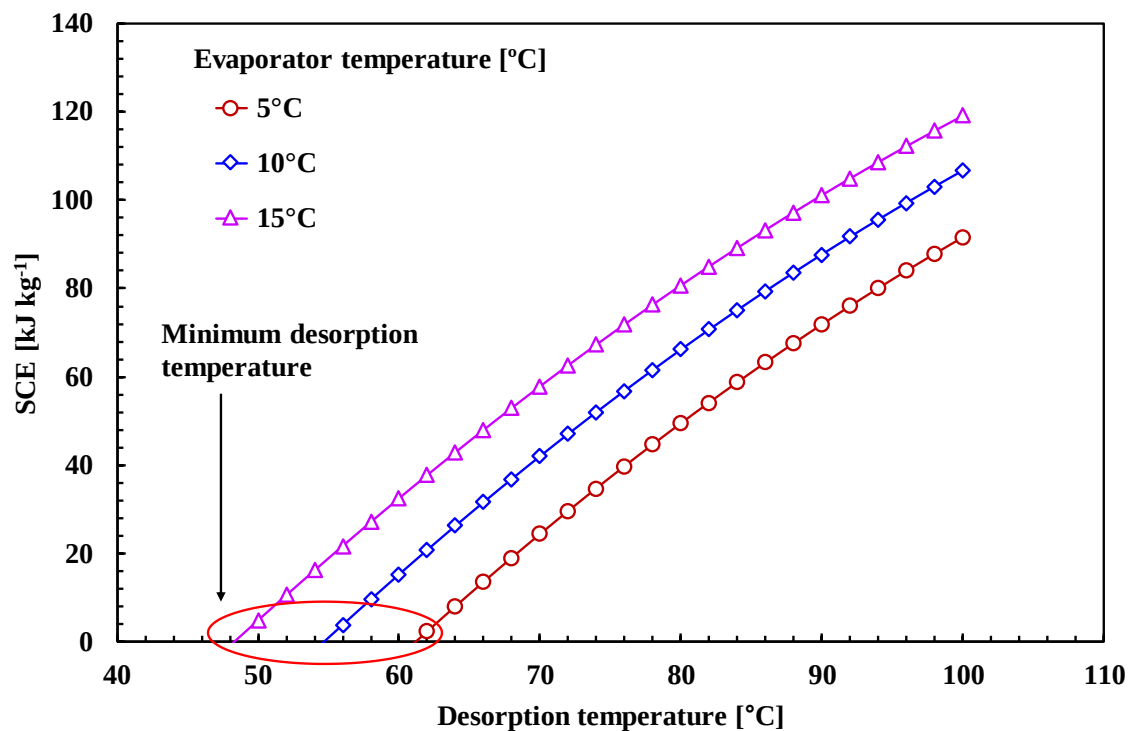


Fig. 6.14 Specific cooling effect (SCE) of WPT-AC (WC500A900K6)/ CO_2 pair with a function of desorption temperature.

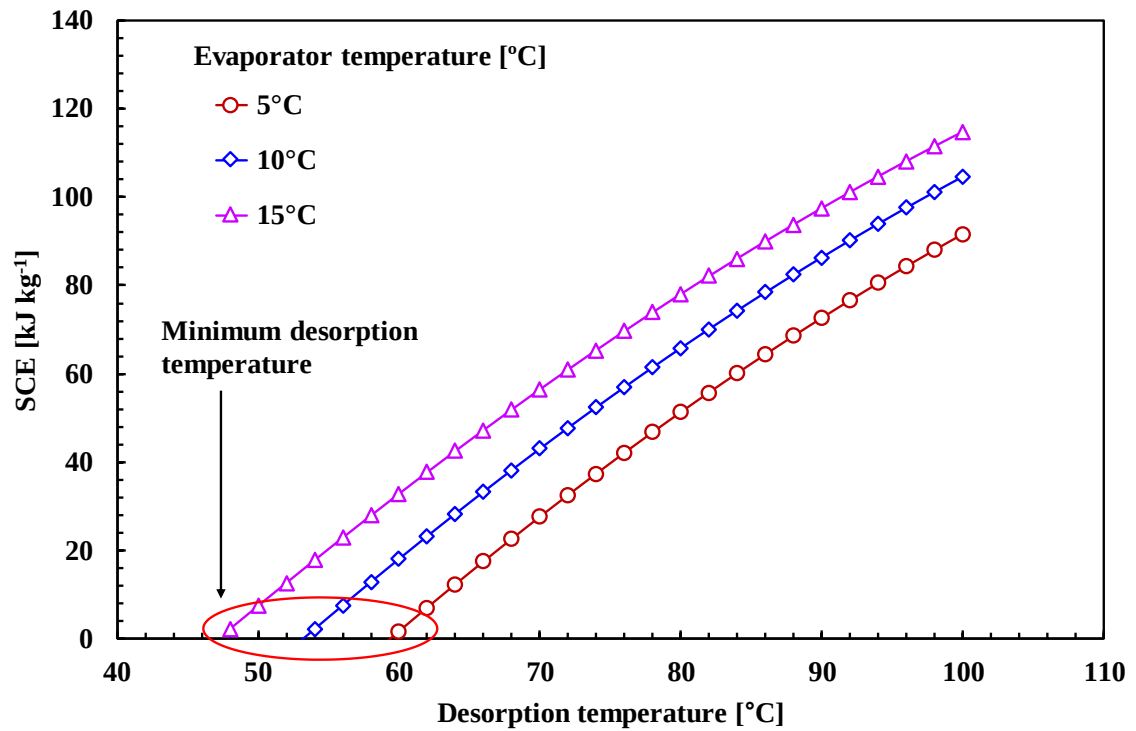


Fig. 6.15 Specific cooling effect (SCE) of M-AC (MC500A900K6)/CO₂ with a function of desorption temperature.

Fig. 6.16 shows the comparison of specific cooling effect (SCE) among biomass-derived ACs/CO₂ and Maxsorb III/CO₂ pairs at evaporator temperature 15°C with the function of desorption temperature. Results show that Maxsorb III/CO₂ adsorption cycle can achieve SCE about 62 kJ kg⁻¹ at evaporation and heat source temperature 15°C and 100°C, respectively. It can be seen that WPT-AC/CO₂ and M-AC/CO₂ both pairs provide very high SCE compared to Maxsorb III/CO₂ in all studied desorption temperatures. It is highlighted that biomass-derived ACs/CO₂ pair provides about 55 to 92% higher SCE compared to Maxsorb III/CO₂ at evaporation temperature 15°C along with heat source temperature 100°C.

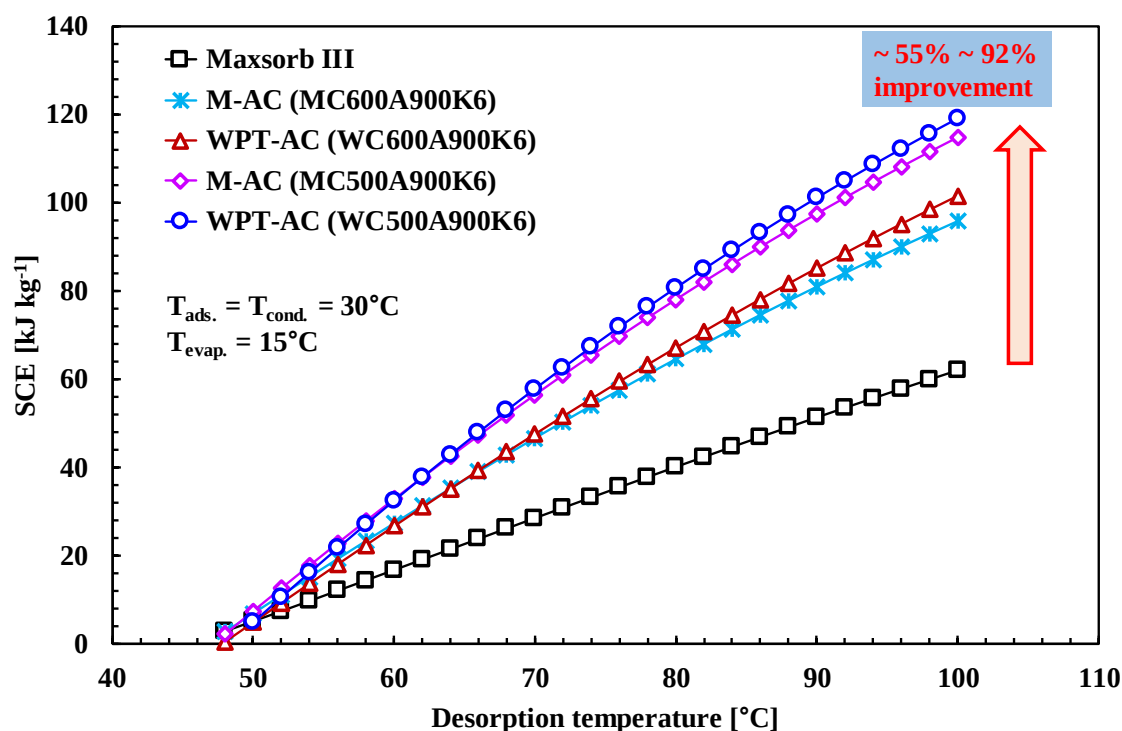


Fig. 6.16 Comparison of specific cooling effect (SCE) among biomass-derived ACs/CO₂ and Maxsorb III/CO₂ pair at evaporator temperature 15°C with the a function of desorption temperature.

The COP values variation of ACs/CO₂ pairs as a function of evaporator and desorption temperature shows the similar characteristic as discussed in case of ACs/ethanol pairs. The COP for biomass-derived ACs/CO₂ pair is also higher than that of Maxsorb III/CO₂ as can be seen in Fig. 6.17. The Maximum COP for Maxsorb III/CO₂ pair is 0.12, however, 0.14 is for C600 ACs and 0.16 is for C500 ACs (Fig. 6.17) at evaporation and desorption temperature 15 and 100°C, respectively.

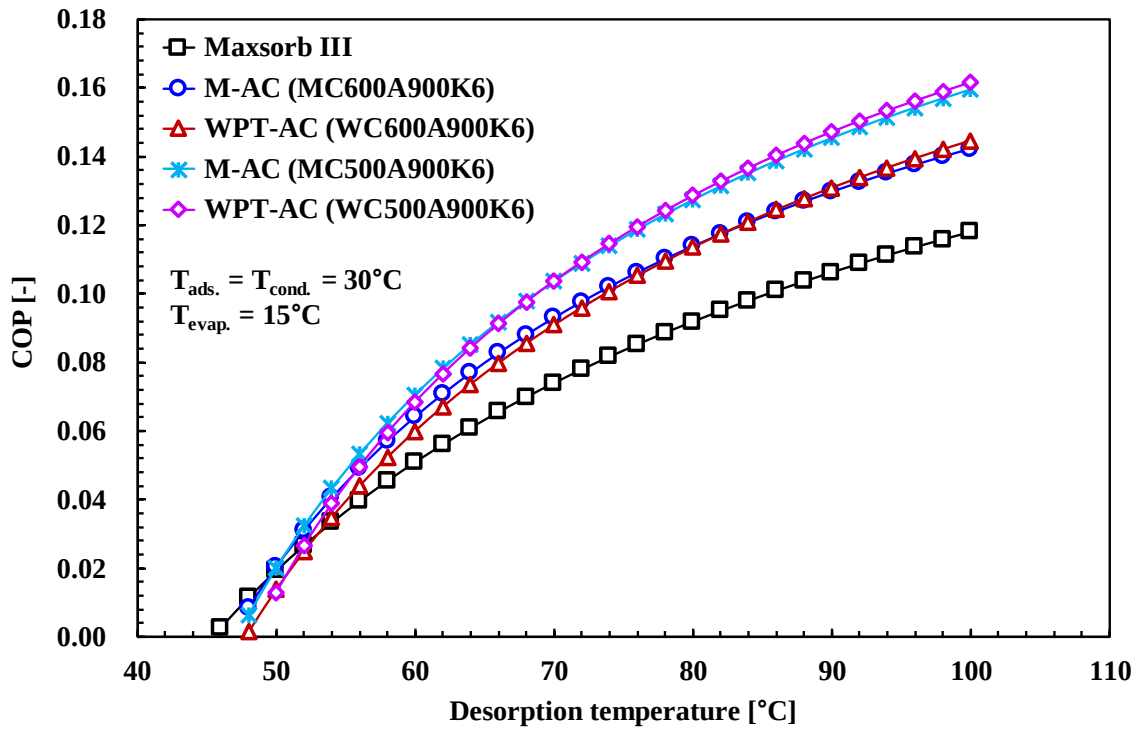


Fig. 6.17 Comparison of COP between biomass-derived ACs and Maxsorb III at evaporator temperature 15°C with the function of desorption temperature.

6.3.2.2 Composite adsorbents

In this section, four composite samples: one is just PVA+AC, one is EG contained, and other two is GNPs contained composites are employed for calculating SCE of the CO₂ based cooling system. The porous properties and adsorption characteristics of CO₂ onto those samples have already been discussed in chapter 3 and 5. The volumetric cooling effect (CE_v) is also calculated for all composites/CO₂ pairs and compared with the parent adsorbent Maxsorb III. A representative illustration of SCE of composite 1 (90 wt% Maxsorb III + 10 wt% PVA)/CO₂ pair with the function of desorption temperature is shown in Fig. 6.18. Here is also found similar characteristics trend line as discussed for ACs/CO₂ pair in the previous section. Comparison of volumetric cooling effect (CE_v) among all studied composites/CO₂ and Maxsorb III/CO₂ pairs at evaporator temperature 15°C with a function of desorption temperature is depicted in Fig. 6.19. It is found that composite 2 (H-grade GNPs)/CO₂ shows higher CE_v than others pairs. This is because of higher adsorption uptake and packing density.

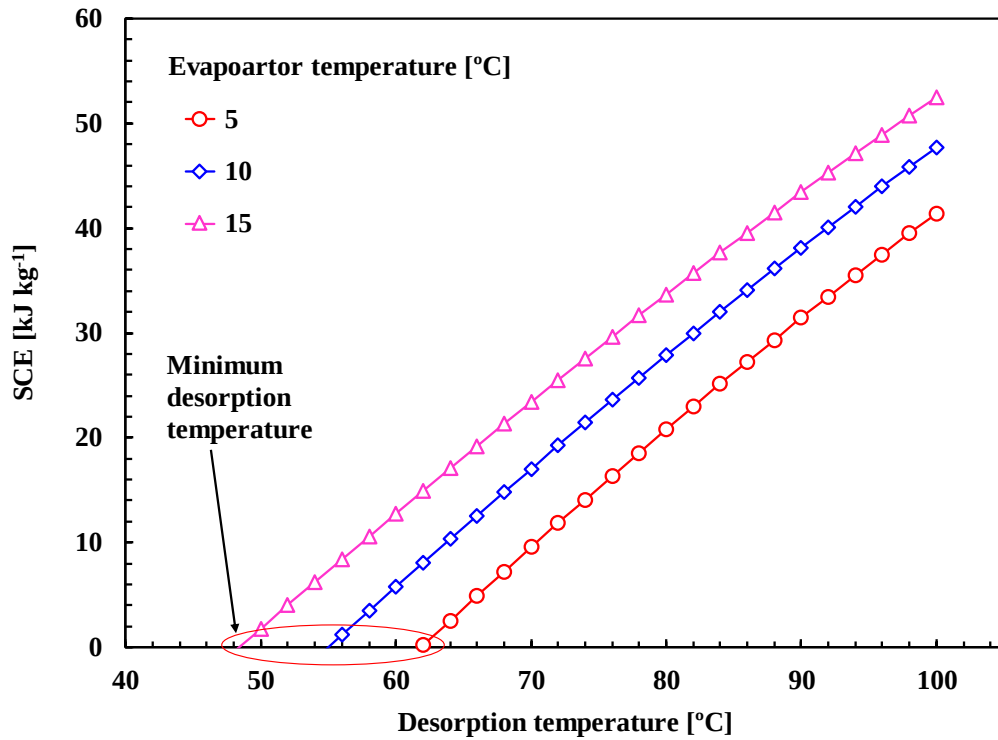


Fig. 6.18 A representative illustration of SCE of composite 1(90 wt% Maxsorb III + 10 wt% PVA)/CO₂ pair with the function of desorption temperature.

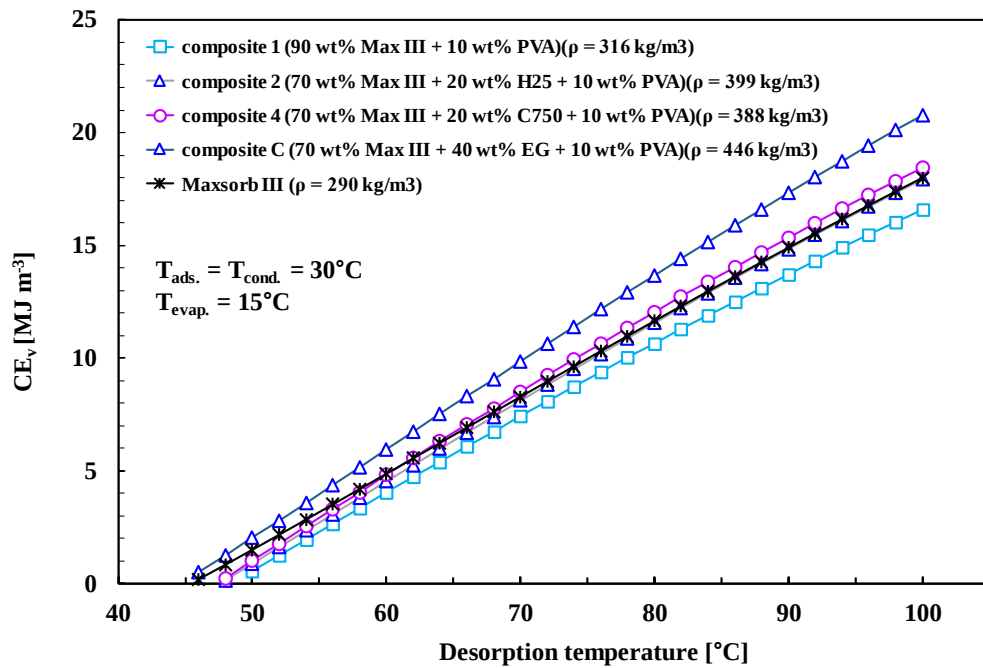


Fig. 6.19 Comparison of volumetric cooling effect (CE_v) among all studied composites/CO₂ and Maxsorb III/CO₂ pairs at evaporator temperature 15 $^{\circ}\text{C}$ with the function of desorption temperature.

6.4 Comparison of thermodynamic parameters

For the sake of comparison, the performance of adsorption cooling cycles employing ten adsorbents/ethanol and nine/CO₂ pairs are furnished in Table 6.1 for evaporation and adsorption temperature 5°C and 30°C, respectively with desorption temperature 80°C and 100°C.

Table 6.1 Adsorption uptake and cycle performance of the studied adsorbents using ethanol and CO₂ for cooling applications.

Adsorbent/adsorbate pair		Desorption temperature							
		80°C				100°C			
		W_{max}	W_{min}	SCE	COP	W_{max}	W_{min}	SCE	COP
		[kg kg ⁻¹]	[kg kg ⁻¹]	[kJ kg ⁻¹]	[-]	[kg kg ⁻¹]	[kg kg ⁻¹]	[kJ kg ⁻¹]	[-]
Ethanol	WC600A900K6	0.787	0.257	465	0.658	0.787	0.078	623	0.686
	MC600A900K6	0.832	0.292	474	0.655	0.832	0.087	654	0.688
	composite A	0.398	0.148	211	0.659	0.398	0.040	306	0.696
	composite C	0.523	0.200	283	0.697	0.523	0.060	406	0.736
	composite 1	0.709	0.325	337	0.677	0.709	0.121	516	0.727
	composite 2	0.557	0.244	275	0.662	0.557	0.085	415	0.708
	composite 3	0.410	0.184	198	0.647	0.410	0.066	302	0.695
	composite 4	0.579	0.259	281	0.647	0.579	0.093	426	0.693
	PIL composite	0.701	0.288	363	0.692	0.701	0.092	535	0.737
	Maxsorb III	0.805	0.391	363	0.660	0.805	0.159	567	0.713
CO ₂	WC500A900K6	1.631	1.228	49	0.098	1.631	0.886	92	0.137
	WC600A900K6	1.578	1.230	43	0.883	1.578	0.923	81	0.125
	MC500A900K6	1.622	1.204	51	0.101	1.622	.876	92	0.138
	MC600A900K6	1.497	1.141	44	0.092	1.497	0.862	78	0.125
	composite C	0.867	0.681	23	0.076	0.867	0.539	40	0.100
	composite 1	1.055	0.886	21	0.066	1.055	1.055	0.718	0.099
	composite 2	0.886	0.734	19	0.068	0.886	0.592	36	0.100
	composite 4	0.897	0.732	20	0.071	0.897	0.585	38	0.102
	Maxsorb III	1.204	0.970	29	0.080	1.204	0.775	53	0.108

6.5 Conclusions

Ethanol as a refrigerant: It is observed that higher evaporator temperature gives higher cooling effect and increases linearly with the increases of desorption temperature for all studied adsorbent/ethanol pairs. It is found that WPT-AC/ethanol adsorption cycle can achieve SCE about 1067 kJ kg^{-1} at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC/ethanol pair provides about 1036 kJ kg^{-1} . It is found that Maxsorb III/ethanol adsorption cycle can achieve SCE about 782 kJ kg^{-1} at same operating conditions. It can be seen that WPT-AC/ethanol and M-AC/ethanol both pairs provide very high SCE compared to Maxsorb III/ethanol in the studied desorption temperatures. It is highlighted that WPT-AC/ethanol adsorption cycle shows 36% higher SCE whilst M-AC/ethanol pair gives about 32% higher SCE compared to Maxsorb III/ethanol at evaporation temperature 15°C along adsorption and heat source 100°C , respectively. The maximum COP of WPT-AC/ethanol and M-AC/ethanol based cooling systems are found to be 0.75 and 0.74, respectively. However, study shows that there is no significant COP difference among the biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs. It can be seen that polymerized IL binder contained composite/ethanol pair shows higher SCE than any other composites and followed by composite 1, composite C, composite 4, composite 2, composite A, and composite 3. The maximum COP for PIL composite/ethanol pair is also found 0.8. In addition, there is a decent agreement between the calculated and theoretical minimum desorption temperature for all ethanol pairs

CO₂ as a refrigerant: It is found that WPT-AC (C500)/CO₂ adsorption cycle can achieve SCE about 119 kJ kg^{-1} at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC (C500)/ethanol pair provides about 115 kJ kg^{-1} . Results show that Maxsorb III/CO₂ adsorption cycle can achieve SCE about 62 kJ kg^{-1} at evaporation and heat source temperature 15°C and 100°C , respectively. It is highlighted that biomass-derived ACs/CO₂ pair provides about 55 to 92% higher SCE compared to Maxsorb III/CO₂ at evaporation temperature 15°C along with heat source temperature 100°C . The COP for biomass-derived ACs/CO₂ pair is also higher than that of Maxsorb III/CO₂ and the maximum COP for Maxsorb III/CO₂ pair is 0.12, however, 0.14 is for C600 ACs and 0.16 is for C500 ACs at evaporation and desorption temperature 15 and 100°C , respectively. It is found that composite 2 (H-grade GNPs)/CO₂ shows higher volumetric cooling effect (CE_v) than other pairs.

Chapter 7

Overall conclusions and recommendations

7.1 Overall conclusions

The main objective of this thesis is to develop high performance activated carbons and composite adsorbents for adsorption heat pump applications. The synthesis process focuses to increase porous properties of ACs from waste biomasses and to enhance the thermal conductivity in order to improve the system performance. The significant findings of this research are summarized as follows:

Biomass-derived ACs:

- i.) In this thesis, ACs of high BET surface and large pore volume is prepared from two biomass precursors (waste palm trunk and mangrove). The study found that carbonization temperature at 500 and 600°C is the optimum condition to obtain the activated carbons with high carbon and yield content.
- ii.) Twelve activated carbon samples from WPT and mangrove have been prepared by changing carbonization, activation temperature and KOH ratios. KOH is used as a chemically activating agent.
- iii.) The synthesized biomass-derived ACs show BET surface area between 1400-3000 m² g⁻¹ having 0.65 to 2.87 cm³ g⁻¹ pore volume. The highest surface area and pore volume of WPT-derived ACs are found to be 2927 m² g⁻¹ (WC600A900K6) and 2.87 cm³ g⁻¹ (WC500A900K6) whilst 2924 m² g⁻¹ (MC600A900K6) and 2.68 cm³ g⁻¹ (MC500A900K6) are for M-derived AC. This surface area and pore volume are the benchmark of any other ACs.
- iv.) Experimental results show that thermal conductivity values vary from 0.054 to 0.041 W m⁻¹ K⁻¹ for WPT-derived ACs whilst 0.061 to 0.045 W m⁻¹ K⁻¹ are for M-derived ACs.
- v.) Adsorption uptake and kinetics of ethanol vapor onto WPT-AC (WC600A900K6) and M-AC (MC600A900K6) have been measured gravimetrically at adsorption temperatures between 30 and 70°C. Four popular adsorption isotherm models and two adsorption kinetics equations

have been employed to correlate the experimental data. Among them, Dubinin Astakhov (D-A) and Tóth equations agree well with the experimental data for both adsorbents. It is also found that WPT-AC shows maximum uptake and can adsorb up to 1.9 kg kg^{-1} whilst one kg of M-AC is able to adsorb 1.65 kg of ethanol. Further, the net ethanol uptake for both the biomass-derived-ACs is found to be similar for a real adsorption heat pump and about 35% higher than the net uptake of Maxsorb III. It is observed that WPT-AC/ethanol pair shows faster kinetics than M-AC/ethanol pair. The calculated activation energy of WPT-AC/ethanol and M-AC/ethanol pairs are $309.62 \text{ kJ kg}^{-1}$ and $467.30 \text{ kJ kg}^{-1}$, respectively.

- vi.) Adsorption of CO_2 onto biomass-derived four AC samples has been measured at adsorption temperatures 25 to 70°C with pressure up to 7 MPa. It is found that Tóth and modified D-A model fit well with the experimental data within $\pm 5\%$ root-mean-square deviation (RMSD). The maximum absolute uptake is found about $2.6 \text{ cm}^3 \text{ g}^{-1}$ for WC500/ CO_2 pair followed by $2.4 \text{ cm}^3 \text{ g}^{-1}$, $2.3 \text{ cm}^3 \text{ g}^{-1}$, and $2.1 \text{ cm}^3 \text{ g}^{-1}$ for MC500, WC600, and MC600/ CO_2 pair, respectively. It should be highlighted that biomass-derived ACs show very high adsorption uptake which is about 40% to 73% higher when compared to Maxsorb III/ CO_2 pair because of their high pore volume. Furthermore, isosteric heat of adsorption (Q_{st}) is also lower for biomass-derived ACs that is good for cooling applications. In addition, all biomass-derived ACs shows a high percentage of ΔW improvement compared to Maxsorb III and Norit RB3 and which is found 176% and 506% higher compared to Maxsorb III and Norit RB3, respectively. There is no significant difference in time constant for reaching 63% of its equilibrium adsorption uptake among the WPT-AC and M-AC samples. The absolute adsorption rate of CO_2 onto biomass-derived ACs is higher than Maxsorb III and among them, WPT-AC (C600) is the highest followed by WPT-AC(C500), M-AC (C500) and M-AC (C600) at a given time.
- vii.) Therefore, biomass-derived ACs are found very potential for ethanol and CO_2 based adsorption systems. Among all the synthesized ACs, WC500A900K6, WC600A900K6, MC500A900K6, and MC600A900K6 are highly recommended as a promising adsorbent for AHP applications.

Furthermore, utilizing of biomass for production of AC is a wise approach in pollution control approach in two ways. Firstly, it can prevent the production of CO₂ or CH₄ by fixing the carbon content of biomass. Secondly, it produces AC, which is industrially useful and environmentally benign materials that can go into the soil and enter natural carbon cycle route. Transformation of biomass wastes into valuable carbon material can also rectify environmental issues like an accumulation of agricultural waste, which causes air and water pollution during the natural degradation process.

EG contained AC composites:

- i.) To enhance the thermal conductivity and volumetric cooling effect, consolidated composite adsorbents, which are combinations of AC (Maxsorb III), expanded graphite (EC500), and PVA binder has been synthesis for development of compact adsorption cooling system. The packing density of composite adsorbents increase with the increase of the percentage of expanded graphite.
- ii.) Among the tested samples, the highest value of thermal conductivity is found to be 0.74 W m⁻¹ K⁻¹ at a composite packing density of 650 kg m⁻³, which is about 11 times higher than that of Maxsorb III powder.
- iii.) It is found that 1 kg of consolidated composite (70% Maxsorb III, 20% EG, 10% binder) able to adsorb 0.89 kg of ethanol whilst adsorption capacity of adsorbent composite A (50% Maxsorb III, 40% EG, 10% binder) is 0.61 kg kg⁻¹, which are about 74% and 50% of the maximum adsorption uptake of Maxsorb III/ethanol pair, respectively. This is clear evidence that the binder does not sacrifice the adsorption capacity of Maxsorb III of consolidated composites. In addition, the volumetric uptake difference of composite C/ethanol pair is about 21% higher than that of Maxsorb III/ethanol.
- iv.) Adsorption of CO₂ onto a composite C (70% Maxsorb III, 30% EG, 10% binder) has been experimentally investigated at three different adsorption temperatures namely, 30, 50, and 70°C and pressures up to 7 MPa. The measured adsorption isotherms data have been successfully fitted with the Langmuir, Tóth, and modified Dubinin-Astakhov (D-A) equation. The isosteric heat of adsorption of studied composite C/CO₂ pair is found to be 22.5 kJ mol⁻¹.

GNPs contained AC composites:

- i.) A series of consolidated AC composites are synthesized employing graphene nanoplatelets (GNPs) as a thermal conductivity enhancer and polyvinyl alcohol (PVA) as a binder. With the same composition ratios, composite 4 shows higher BET surface and pore volume compared to composite 2 because porous properties of C750 is higher than H25.
- ii.) Thermal diffusivity, as well as thermal conductivity, increases by introducing GNPs into the AC and binder. Experimental results show that H-grade GNPs is superior for enhancing the thermal conductivity of AC composite compared to C-grade. The adding of both the GNPs in the composite increases the packing density. Furthermore, the thermal conductivity increases with the increasing of packing density and the highest thermal conductivity are found $1.55 \text{ W m}^{-1} \text{ K}^{-1}$ for composite 3 at packing density of 614 kg m^{-3} , which is about 23.5 times higher than AC powder.
- iii.) Ethanol adsorption isotherms onto the all synthesized GNPs composites are measured using high precision adsorption measurement unit. Ethanol adsorption uptake is higher for composite 1 followed by composite 4, 2 and 3. This due to the high BET surface area and pore volume of composite 1. The effective equilibrium volumetric uptake (kg m^{-3}) of all composites show higher compared to Maxsorb III. The highest improvement is observed for composite 2, which is about 23%. The consolidated composite shows a lower absolute rate of ethanol uptake than a parent. However, GNPs contained composites show almost the same absolute rate. In the viewpoints of all studied aspects (thermal diffusivity/conductivity, instantaneous and equilibrium uptake, packing density and effective volumetric uptake), this study concludes the composite 3 could be the optimal choice followed by composite 2. Therefore, enhanced thermal conductivity and adsorption characteristics of the synthesized GNPs contained AC composites are important for designing a compact next-generation activated carbon/ethanol based adsorptive cooling systems.

- iv.) The CO₂ adsorption characteristics onto GNPs contained composite 1, 2, and 4 are measured thermogravimetric method at adsorption temperatures 30-70°C and pressure up to 5 MPa. The experimental data are fitted with Tóth and modified D-A isotherm model and found good agreement between the experimental and predicted data. It is found that composite 1 possess higher adsorption capacity of CO₂ compared to all other composites because it contains a higher amount of Maxsorb III. In addition, C-grade GNPs contained composite 4 shows slightly higher adsorption uptake than that of H-grade contained composite 2, although both composites contain the same composition of additives materials. This phenomenon might be attributed to the higher porous properties of C-grade GNPs than H-grade. It is noticed that composite 1 can adsorb CO₂ about 1.4331 cm³ g⁻¹ whilst 1.1880 cm³ g⁻¹ and 1.2181 cm³ g⁻¹ are for composite 2 and 4, respectively. The adsorption uptake variation with time shows there is no significant time difference among all the composites/CO₂ pairs to reach of its any equilibrium uptake value.
- v.) Consolidated composites with higher thermal conductivity and volumetric uptake could improve the system performance and reduce the size. With the advent of the technological improvement for heat exchangers, composite adsorbent materials can be packed inside the adsorber/desorber heat exchanger, which will lead to notable performance improvement in adsorption cooling and heat pump systems.

AC composite using PIL binder:

- i.) The use of polymerized IL as a potential binder in the synthesis of consolidated AC composite for AHP applications has been explored for the first time. PIL named as vinylbenzyltrimethyl ammonium alanate [VBTMA][Ala] (10 wt%) is used for binding AC. The surface area and pore volume of PIL composite increase by more than 11% and 18%, respectively, as compared to the PVA composite. In addition, the thermal conductivity of PIL composite exhibits 0.122 W m⁻¹ K⁻¹ which is about 85% higher than that of Maxsorb III.

- ii.) Composite using PIL as a binder shows also promising for ethanol adsorption. The volumetric uptake is estimated using the packing density of PIL composite which has the ability to adsorb about 388 kg m^{-3} of ethanol at an adsorption temperature of 30°C whilst Maxsorb III can adsorb ethanol as high as 348 kg m^{-3} at the same adsorption temperature. For a typical operating condition of AHP system, composite using polymerized IL as a binder showed 22% higher net ethanol uptake than the net uptake of parent material Maxsorb III.

Equilibrium thermodynamic performance of adsorbent/refrigerant pairs:

- i.) **Ethanol as a refrigerant:** It is found that WPT-AC/ethanol adsorption cycle can achieve SCE about 1067 kJ kg^{-1} at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC/ethanol pair provides about 1036 kJ kg^{-1} . It is emphasized that WPT-AC/ethanol adsorption cycle shows 36% higher SCE whilst M-AC/ethanol pair gives about 32% higher SCE compared to Maxsorb III/ethanol at evaporation temperature 15°C along adsorption and heat source 100°C , respectively. The maximum COP of WPT-AC/ethanol and M-AC/ethanol based cooling systems are found to be 0.75 and 0.74, respectively. However, study shows that there is no significant COP difference among the biomass-derived ACs/ethanol and Maxsorb III/ethanol pairs. It can be seen that polymerized IL contained composite/ethanol pair shows higher SCE than any other composites and followed by composite 1, composite C, composite 4, composite 2, composite A and composite 3. The maximum COP for PIL composite/ethanol pair is also found 0.8. In addition, there is a decent agreement between the calculated and theoretical minimum desorption temperature for all ethanol pairs.
- ii.) **CO₂ as a refrigerant:** It is found that WPT-AC (C500)/CO₂ adsorption cycle can achieve SCE about 119 kJ kg^{-1} at evaporation temperature 15°C along with heat source temperature 100°C whilst M-AC (C500)/ethanol pair provides about 115 kJ kg^{-1} . It is highlighted that biomass-derived ACs/CO₂ pair provides about 55 to 92% higher SCE compared to Maxsorb III/CO₂ at evaporation temperature 15°C along with heat source temperature 100°C . The COP for biomass-derived ACs/CO₂ pair is also higher than that of Maxsorb

III/CO₂ and the maximum COP for Maxsorb III/CO₂ pair is 0.12, however, 0.14 is for C600 ACs and 0.16 is for C500 ACs at evaporation and desorption temperature 15 and 100°C, respectively. It is found that composite 2 (H-grade GNPs)/CO₂ shows higher volumetric cooling effect (CE_v) than that of other pairs.

7.2 Recommendations

The following recommendations are made by the author for further studies related to the topics covered in this thesis:

- a) Detailed dynamic system simulation using biomass-derived ACs/ethanol and CO₂ pairs and composite adsorbent/ethanol and CO₂ pairs for adsorption heat pump applications.
- b) Study on biomass-derived ACs based composites for AHP systems.
- c) Development of a technique to incorporate the composites into the heat exchanger.
- d) To explore in depth and more of polymerized ionic liquid (PIL) for making composite adsorbents.
- e) To investigation of gas permeability into the consolidated composites.
- f) To do a surface treatment of biomass-derived ACs and additives materials for composites using functional groups for further improvement of uptake and thermal conductivity.
- g) To perform surface treatment, surface energy and acid-base properties are needed to investigate in details.

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Appendix A. Uncertainty analysis

The uncertainty in ethanol adsorption uptake measurements (kg kg^{-1}) based on the experimental test rig shown in Fig. 4.1 has been estimated using Eq. (A1). The experimentally measured adsorption uptake and the corresponding derivatives are also given by Eqs. A1(a)- A1(d) below;

$$\delta W = \sqrt{\left(\frac{\partial W}{\partial d_{\text{evap}}} \delta d_{\text{evap}}\right)^2 + \left(\frac{\partial W}{\partial m_{\text{comp}}} \delta m_{\text{comp}}\right)^2 + \left(\frac{\partial W}{\partial h_{\text{evap}}} \delta h_{\text{evap}}\right)^2} \quad (\text{A1})$$

$$W = \rho_l h_{\text{evap}} \frac{\pi}{4} \left(\frac{d_{\text{evap}}^2}{m_{\text{comp}}} \right) \quad (\text{A1a})$$

$$\frac{\partial W}{\partial d_{\text{evap}}} = \rho_l h_{\text{evap}} \frac{\pi}{4} \left(\frac{2d_{\text{evap}}}{m_{\text{comp}}} \right) \quad (\text{A1b})$$

$$\frac{\partial W}{\partial m_{\text{comp}}} = -\rho_l h_{\text{evap}} \frac{\pi}{4} \left(\frac{d_{\text{evap}}^2}{m_{\text{comp}}^2} \right) \quad (\text{A1c})$$

$$\frac{\partial W}{\partial h_{\text{evap}}} = \rho_l \frac{\pi}{4} \left(\frac{d_{\text{evap}}^2}{m_{\text{comp}}} \right) \quad (\text{A1d})$$

Where δW presents the uncertainty in the ethanol adsorption uptake measurements, δd_{evap} stands for uncertainty of the evaporator diameter and δm_{evap} is the uncertainty of sample mass measurements whilst δh_{evap} is the uncertainty ethanol level height measurements inside the evaporator using the digital microscope. The symbols d_{evap} , m_{comp} , and h_{evap} represent the diameter of evaporator, composite sample mass, and height of ethanol level inside of the evaporator, respectively. The detailed specifications are as follows; $d_{\text{evap}} = 6.8 \text{ mm}$, $\delta d_{\text{evap}} = 0.15 \text{ mm}$, $m_{\text{comp}} = 1.97 \text{ g}$ and $\delta m_{\text{comp}} = 0.01 \text{ g}$ and $\delta h_{\text{evap}} = 0.01 \text{ mm}$. Using equation (A1), the uncertainty of the ethanol adsorption uptake measurements has been found to be varying from 4.4 to 5.6%.

The surface area and pore size of the studied samples are measured using high accuracy surface characterization analyzer with pressure transducers accuracy of 0.15% of the reading with a resolution to 10^{-5} mmHg . The measurement error range is automatically calculated by the analyzer software and shown in every porous properties tables.

For thermal diffusivity measurements, the sample thickness is measured by using QuantuMike micrometer with resolution of 0.001mm and instrumental error of $\pm 1\mu\text{m}$. The NETZSCH LFA 457 MicroFlash system is used to measure the thermal diffusivity with an accuracy and repeatability of $\pm 3\%$ and $\pm 2\%$, respectively. The thermal diffusivity of each sample has been measured several times, and the standard deviation for the measured data is calculated and varies very little and presented in each plot.

The adsorption uptakes of ethanol and CO_2 are investigated using thermogravimetric analyzer (TGA) unit. The sample weight is directly measured by magnetic suspension balance with $\pm 1\mu\text{g}$ resolution. Mass measurement repeatability of magnetic balance is $\pm 30\mu\text{g}$ with relative error of $\pm 0.002\%$ of the reading. Since the sample mass used in the study is about 40 to 200 mg, so the relative experimental error is always less than 0.001%, which could not be noticeable in error bars.

Appendix B. Surface characterization analyzer (3Flex™)

The analyzer is an automated gas adsorption analyzer with three ports allowing up to three samples to be analyzed simultaneously. The core analytical engine is composed of an advanced vacuum system, a versatile analysis manifold, and sensitive pressure transducers on each analysis port. The basic configuration consists of 2 or 3 micropore ports. Standard ports can be individually upgraded for high quality micropore analyses with 10 torr and 0.1 torr transducers on each micropore port. The analyzer also features a dedicated port for measuring the saturation pressure (P_0) on a continuous basis. Surface areas as low as $0.01 \text{ m}^2 \text{ g}^{-1}$ can be measured using nitrogen and as low as $0.001 \text{ m}^2 \text{ g}^{-1}$ with krypton as the adsorptive. Up to 1000 data points can be collected allowing the observation of minute details of the isotherm. The analyzer must be equipped with a 10 mmHg transducer and a high-vacuum pump to provide this capability. Up to four analyzers can be operated with one computer. The system consists of the analyzer, an optional SmartPrep degasser for preparing samples, a dry diaphragm roughing vacuum pump, and a computer for entering analysis and report options (Fig. B1 and Fig. B2).

MicroActive Reports: MicroActive reports are automatically generated after an analysis is performed. This feature provides a quick and easy way to investigate and manipulate analysis data using a variety of reporting methods. When a sample information file with a status of Complete, Analyzing, or Entered is opened, an iso-therm linear plot and log plot of the data collected during analysis are displayed as well as a summary of the analysis giving the total pore volume. From this window, numerous reports are accessible from a dropdown menu, including:

- BET Surface Area
- Langmuir Surface Area
- t-Plot
- Alpha-S Method
- BJH Adsorption
- BJH Desorption
- Dollimore-Heal Adsorption

- Dollimore-Heal Desorption
- Horvath-Kawazoe
- DFT Pore Size
- DFT Surface Energy
- Dubinin-Radushkevich
- Dubinin-Astakhov

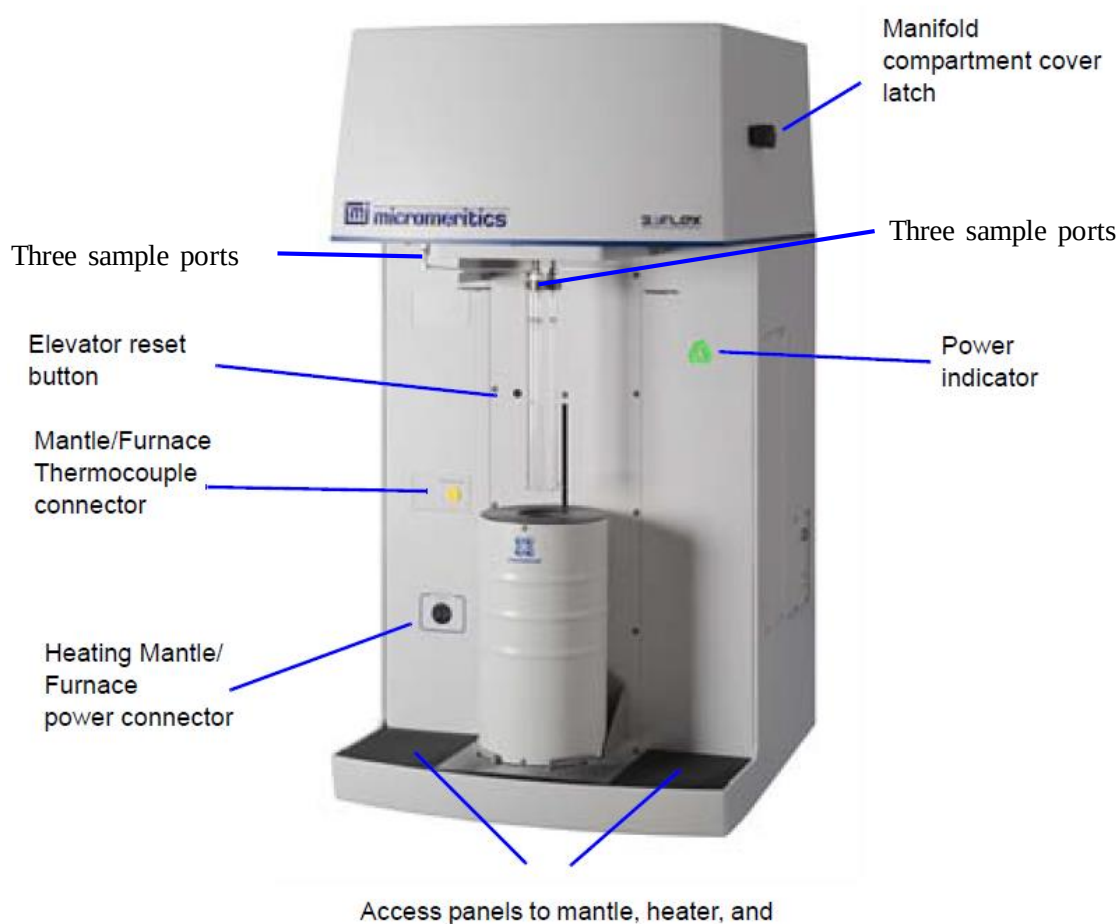


Fig. B1 Photograph of 3Flex instrument.

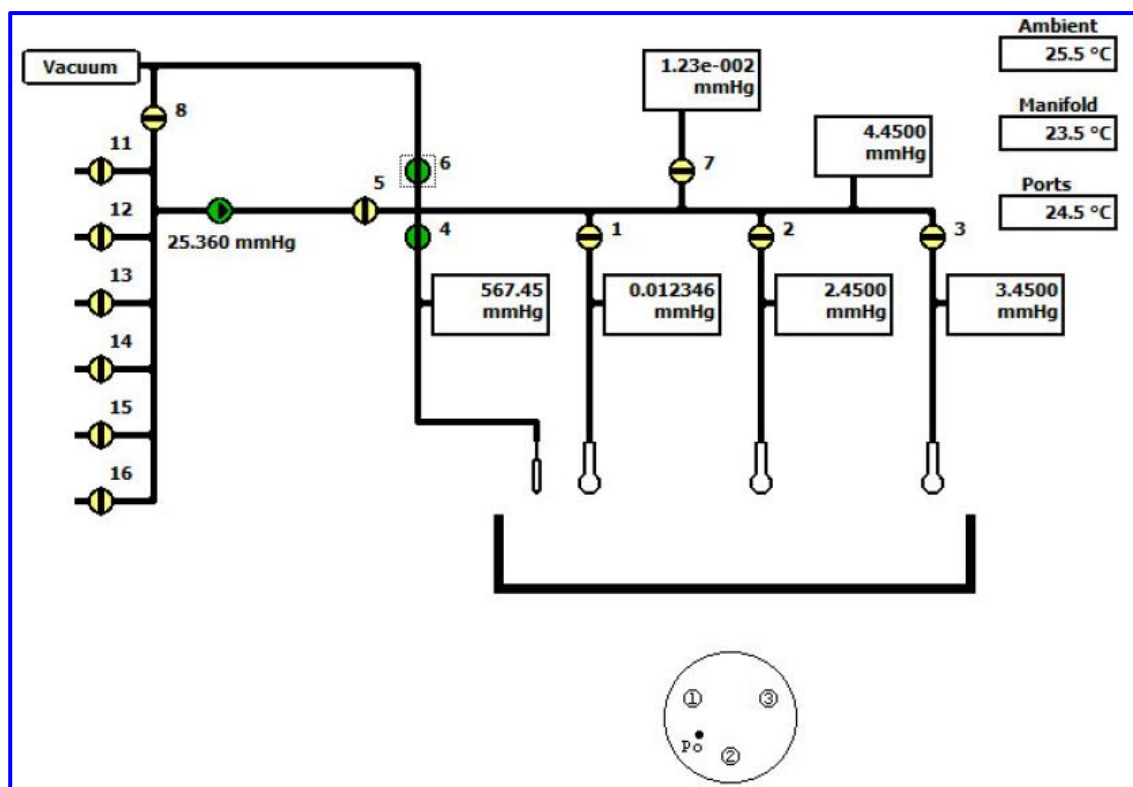


Fig. B2 Schematic drawing of 3Flex instrument.

Appendix C. Thermal diffusivity analyzer (LFA457)-laser flash method

The measuring part is constructed vertically (Fig. C1). The laser system is housed in the lower closed casing. The laser beam emerges vertically at the top. The furnace system can be moved by means of a motor driven hoist in vertical direction. A thermocouple measures the absolute temperature of the sample. This thermocouple is mounted on the sample holder and is located at the height of the sample. The temperature increase on rear face of the sample is measured by means of an IR (infrared) sensor. The sensor material is cooled by liquid nitrogen.

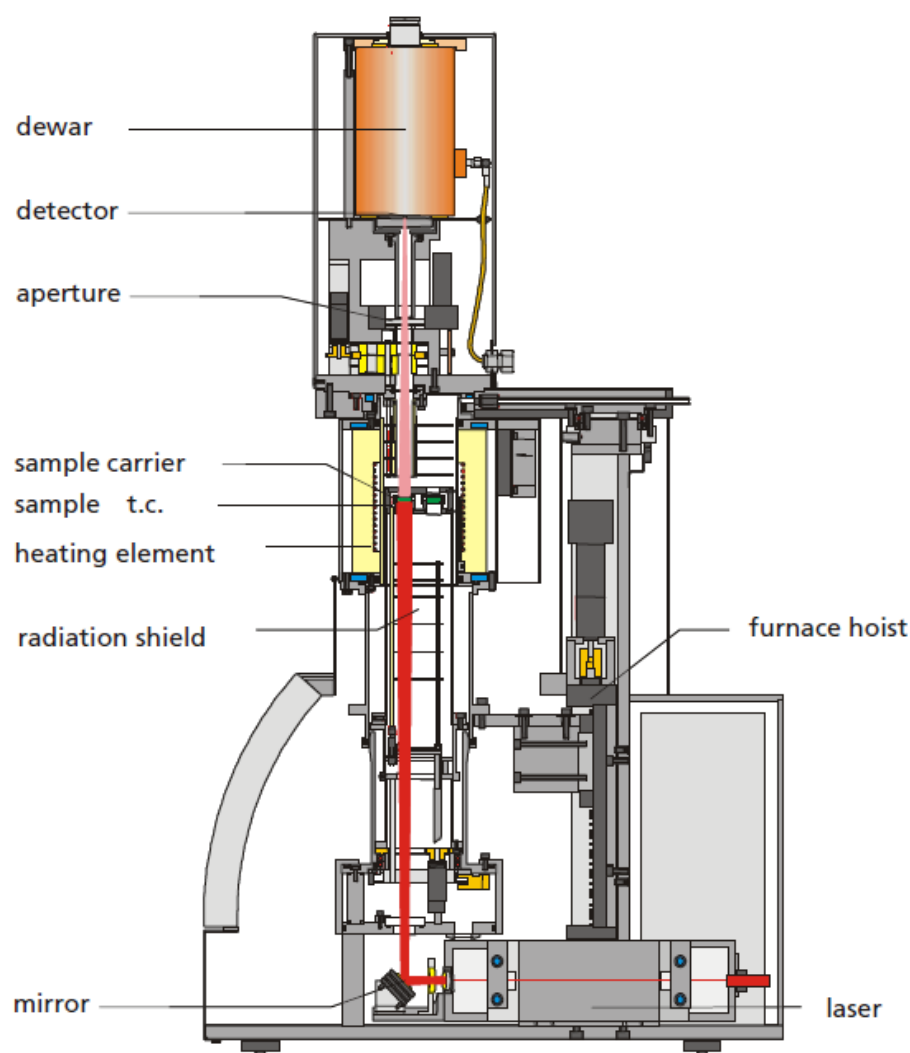


Fig. C1 Schematic diagram of LFA 457 microflash system.

The vertical installation of laser and IR sensor allows very easy sample holder handling. The sample holder (Fig. C2) is in a horizontally stable and therefore defined position. Once the detector has been swung to the side, the sample holder is directly accessible and can be inserted or removed easily. The carrier tube upper opening supports the sample tray. This sample tray holds the sample support with the sample inside. The contact between sample and sample support is greatly minimized. The requirement of lowest possible heat loss from the sample has been fulfilled by minimizing the contact between sample support and sample. The inside diameter of the holes in the sample support is constructed as a limiting diaphragm below the sample and corresponds exactly to the diameter of the sample. The impinging laser beam with a larger diameter is exactly masked with the diameter of the sample. A cover, which is placed over both the test piece and the holder as a hood, prevents the emergence of laser diffuse light. In this way, disturbances in the measuring signal of the IR sensor are avoided.

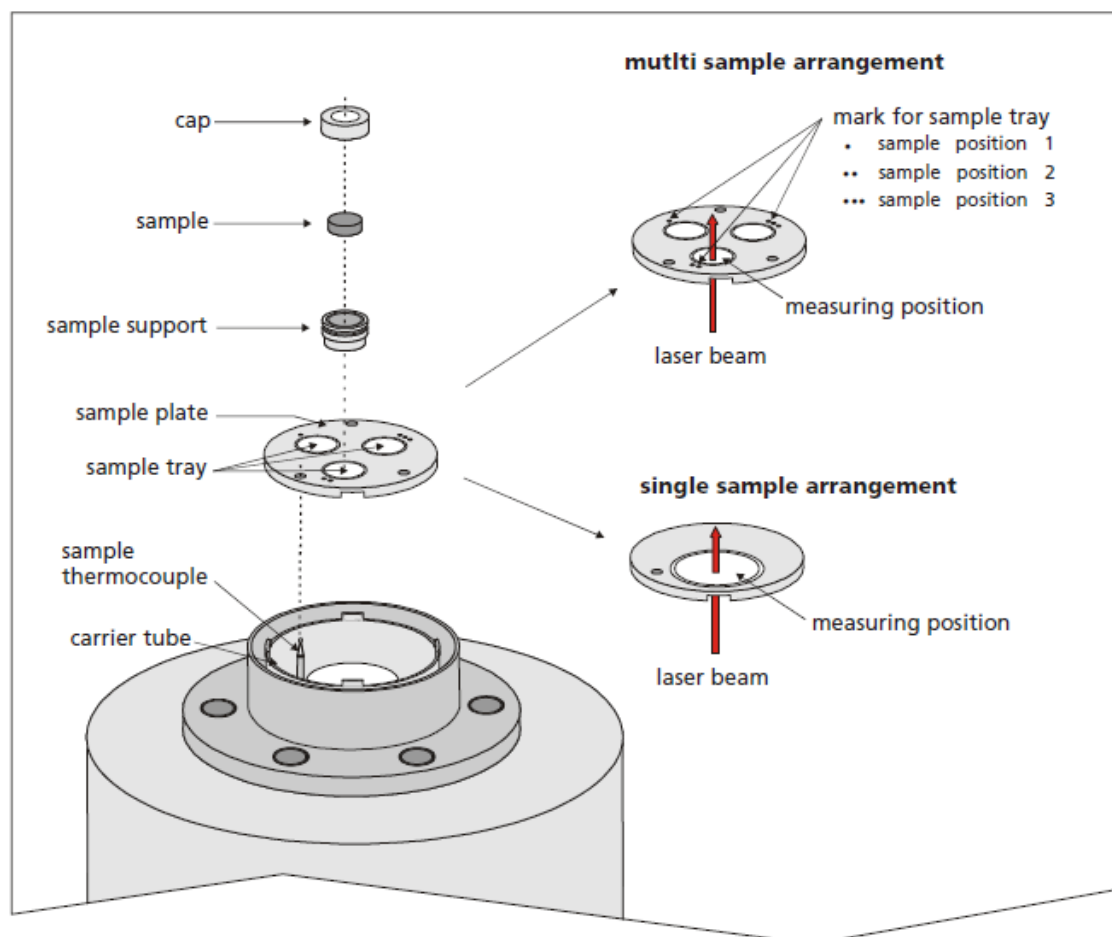


Fig. C2 Sample holder and arrangement inside the LFA 457 system.

Sample Geometries

sample support	diameter/size
multi sample arrangement (big hole)	12.7 mm
multi sample arrangement (small hole)	10 mm, 6mm (available on request)
multi sample arrangement (square)	10 mm x 10 mm (available on request)
single sample arrangement	25.4 mm

Ideal Sample Thickness

therm. diffusivity range	possible sample thickness / mm
Low diffusivity e.g. polymers (0.01 – 1 mm ² /s)	0.05 to 3
Medium diffusivity e.g. ceramics (1 – 50 mm ² /s)	0.5 to 5
High diffusivity e.g. copper (50 – 1200 mm ² /s)	1 to 5

Furnaces

The LFA 457 can be equipped with the following furnaces:

6.257.1-31.0 (high temperature furnace, temperature range: RT – 1100°C)

6.257.1-30.0 (low temperature furnace, temperature range: -125°C – 500°C)

Technical Data

Temperature range	
	-125°C ... 500°C, RT ... 1100°C, (2 exchangeable furnace types) Contactless measurement of temperature rise with IR detector
Heating- and cooling rates	
	0.01 K/min ... 50 K/min
Laser	
	Laser Class: 4 Medium: Nd:Glas Wavelength: 1054 nm Laser pulse energy: up to 18 J Pulse width: ~0.3 ms Alignment laser Class: 1M Medium: laser diode Wavelength: 650 nm Laser energy: max. 5 mW
Measuring range	
	0.01 mm ² /s ... 1000 mm ² /s (thermal diffusivity) Measuring range: 0.1 W/mK ... 2000 W/mK (thermal conductivity)
Detector	
	InSb, RT ... +1100°C MCT, -125 ... +500°C
Sample dimensions	
	10 mm ... 25.4 mm diameter (also 8x8 mm und 10x10 mm, square) 0.1 mm ... 6 mm thickness
Sample holder	
	SiC, graphite Liquid metal holder: sapphire Sample holder for liquids: aluminium, platinum
Atmosphere	
	inert, oxidizing, reducing, static, dynamic Vacuum-tight assembly up to 10 ⁻² mbar (1 Pa)

Appendix D. C-Therm TCi thermal conductivity analyzer- modified transient plane source method

Fig. D1 and Fig. D2 shows the schematic diagram and photograph of TCi thermal conductivity analyzer, respectively. It comprises of a one-sided interfacial heat reflectance sensor, sample cell for measuring powder sample, control unit and computer software. TCi system employs the modified transient plane source (MTPS) for thermal conductivity measurement. The sensor has a central heater/sensor element in the shape of a spiral surrounded by a guard ring, which generates heat in addition to the spiral heater. A known constant current is applied to the sensor's spiral heating element and providing a small amount of heat to the sample. Accordingly, approximating a one-dimensional heats flow from the sensor into the material being tested. The sample is heated by approximately 1-3°C during the testing. Sample absorbs some of the heat depending on its thermal properties, and the rest causes a temperature rise at the sensor interface. Temperature rise causes the voltage drop on the spiral heater. The rate of increase in the sensor voltage is used to determine the thermal properties of the sample. The voltage is factory-calibrated to temperature. The thermal conductivity is inversely proportional to the rate of increase in the temperature at the point of contact between the sensor and the sample. The precision and accuracy of TCi system is better than 1% and 5% respectively.

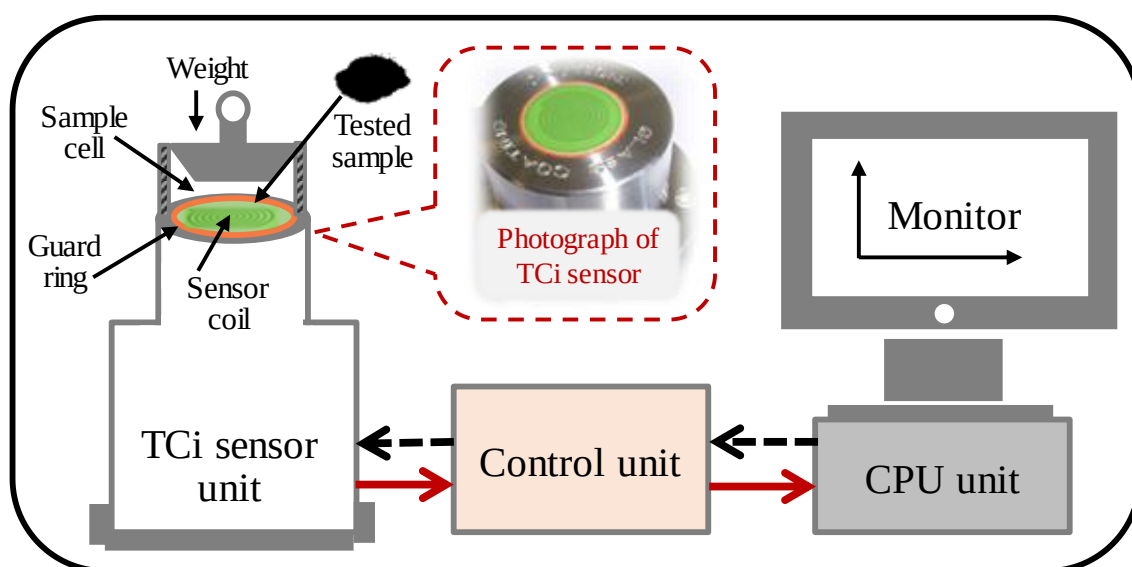


Fig. D1 Schematic diagram of TCi thermal conductivity analyzer.

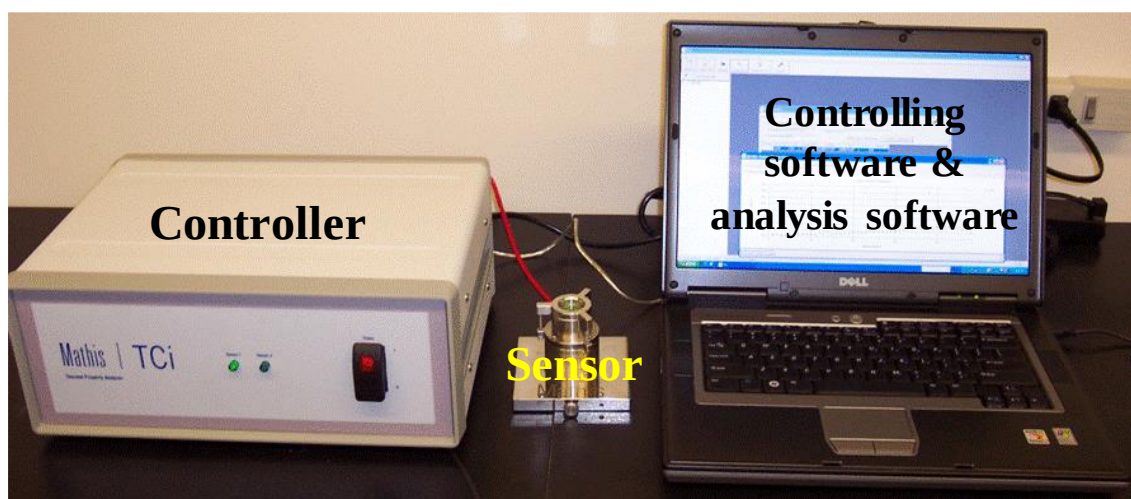


Fig. D2 Photograph of TCi thermal conductivity analyzer.

Appendix E. Experimental uptake of WPT-AC/ethanol

Table E1. Experimental uptake at 30°C.

Step	Tads	Time (sec)	P (kPa)	Uptake (g)	Uptake (g/g)	ZP(g)	MP1-ZP(g)
1	29.94	0.281	1.248051	0.000063	0.001857	5.06643	9.47898
1	29.94	1.201	1.21269	0.013953	0.408831	5.06643	9.49287
1	29.94	2.262	1.25198	0.004833	0.141617	5.06643	9.48375
1	29.94	3.198	1.25198	0.003593	0.105285	5.06643	9.48251
1	29.94	4.212	1.25198	0.002923	0.085654	5.06643	9.48184
1	29.94	5.257	1.244122	0.002493	0.073055	5.06643	9.48141
1	29.94	6.271	1.25198	0.002363	0.069246	5.06643	9.48128
1	29.94	7.301	1.244122	0.002303	0.067488	5.06643	9.48122
1	29.94	8.206	1.248051	0.002253	0.066023	5.06643	9.48117
1	29.94	9.235	1.240193	0.002213	0.064851	5.06643	9.48113
1	29.94	10.218	1.236264	0.002183	0.063972	5.06643	9.4811
1	29.94	12.262	1.240193	0.002173	0.063679	5.06643	9.48109
1	29.94	14.196	1.244122	0.002243	0.06573	5.06643	9.48116
1	29.94	16.24	1.244122	0.002353	0.068953	5.06643	9.48127
1	29.94	18.283	1.236264	0.002543	0.07452	5.06643	9.48146
1	29.94	20.296	1.236264	0.002733	0.080087	5.06643	9.48165
1	29.94	22.23	1.236264	0.002863	0.083896	5.06643	9.48178
1	29.94	24.227	1.236264	0.003063	0.089756	5.06643	9.48198
1	29.94	26.318	1.232335	0.003273	0.095909	5.06643	9.48219
1	29.94	42.23	1.228406	0.004613	0.135171	5.06643	9.48353
1	29.94	44.258	1.232335	0.004763	0.139566	5.06643	9.48368
1	29.94	46.27	1.232335	0.004933	0.144547	5.06643	9.48385
1	29.94	48.36	1.232335	0.005073	0.148649	5.06643	9.48399
1	29.94	50.264	1.232335	0.005223	0.153044	5.06643	9.48414
1	29.94	52.198	1.228406	0.005313	0.155681	5.06643	9.48423
1	29.94	54.351	1.228406	0.005473	0.160369	5.06643	9.48439
1	29.94	56.192	1.228406	0.005573	0.163299	5.06643	9.48449
1	29.94	58.22	1.228406	0.005683	0.166522	5.06643	9.4846
1	29.94	60.295	1.228406	0.005843	0.171209	5.06643	9.48476
1	29.94	66.332	1.228406	0.006173	0.180878	5.06643	9.48509
1	29.94	68.266	1.228406	0.006273	0.183808	5.06643	9.48519
1	29.94						
1	29.94	630.213	1.220548	0.012523	0.366932	5.06643	9.49144
1	29.94	635.189	1.224477	0.012533	0.367225	5.06643	9.49145

Table E1. Experimental uptake at 30°C (continued).

Step	Tads	Time (sec)	P (kPa)	Uptake (g)	Uptake (g/g)	ZP(g)	MP1- ZP(g)
2	30.08	0.281	1.660593	0.01311	0.38413	5.06645	9.49165
2	30.08	1.108	1.656664	0.01311	0.38413	5.06645	9.49165
2	30.08	2.138	1.660593	0.01311	0.38413	5.06645	9.49165
2	30.08	3.261	1.660593	0.01312	0.384423	5.06645	9.49166
2	30.08	4.119	1.664522	0.01313	0.384716	5.06645	9.49167
2	30.08	5.148	1.668451	0.01317	0.385888	5.06645	9.49171
2	30.08	6.147	1.660593	0.01319	0.386474	5.06645	9.49173
2	30.08	7.176	1.664522	0.01324	0.387939	5.06645	9.49178
2	30.08	8.159	1.664522	0.01327	0.388818	5.06645	9.49181
2	30.08	9.173	1.668451	0.01332	0.390283	5.06645	9.49186
2	30.08	10.109	1.660593	0.01335	0.391162	5.06645	9.49189
2	30.08	12.137	1.668451	0.01342	0.393213	5.06645	9.49196
2	30.08	14.181	1.660593	0.0135	0.395557	5.06645	9.49204
2	30.08	16.115	1.664522	0.01357	0.397608	5.06645	9.49211
2	30.08	18.159	1.668451	0.01363	0.399366	5.06645	9.49217
2	30.08	20.187	1.668451	0.0137	0.401417	5.06645	9.49224
2	30.08	22.137	1.668451	0.01374	0.402589	5.06645	9.49228
2	30.08	24.149	1.668451	0.0138	0.404347	5.06645	9.49234
2	30.08	26.162	1.67238	0.01387	0.406398	5.06645	9.49241
2	30.08	28.143	1.668451	0.01392	0.407863	5.06645	9.49246
2	30.08	30.171	1.660593	0.01399	0.409914	5.06645	9.49253
2	30.08	32.105	1.656664	0.01404	0.411379	5.06645	9.49258
2	30.08	34.149	1.664522	0.0141	0.413137	5.06645	9.49264
2	30.08	36.161	1.668451	0.01416	0.414895	5.06645	9.4927
2	30.08	38.205	1.664522	0.0142	0.416067	5.06645	9.49274
2	30.08	40.171	1.664522	0.01426	0.417825	5.06645	9.4928
2	30.08	42.105	1.664522	0.0143	0.418997	5.06645	9.49284
2	30.08	92.213	1.664522	0.01523	0.446245	5.06645	9.49377
2	30.08	94.272	1.668451	0.01525	0.446831	5.06645	9.49379
2	30.08						
2	30.08	385.136	1.660593	0.01722	0.504552	5.06645	9.49576
2	30.08	390.128	1.664522	0.01723	0.504845	5.06645	9.49577
2	30.08	610.167	1.668451	0.01773	0.519495	5.06645	9.49627
2	30.08	615.299	1.668451	0.01773	0.519495	5.06645	9.49627
2	30.08	620.12	1.668451	0.01774	0.519788	5.06645	9.49628
2	30.08	625.128	1.660593	0.01774	0.519788	5.06645	9.49628
2	30.08	630.12	1.664522	0.01776	0.520374	5.06645	9.4963
2	30.08	635.268	1.660593	0.01776	0.520374	5.06645	9.4963
2	30.08	640.119	1.656664	0.01777	0.520667	5.06645	9.49631

Appendix F. Experimental uptake of composite C/CO₂

Table F1. Experimental uptake at 30°C.

Step	Tads	Time (sec)	P (kPa)	Uptake (g)	Uptake (g/g)	ZP(g)	MP1-ZP (g)
1	30.08	0.265	3922.265	0.199385	0.973958	5.35008	9.7416
1	30.08	1.17	589.7427	0.308875	1.508796	5.35008	9.8511
1	30.08	2.106	627.465	0.187065	0.913777	5.35008	9.7292
1	30.08	3.245	721.6307	0.186575	0.911383	5.35008	9.7288
1	30.08	4.165	780.1381	0.186245	0.909771	5.35008	9.7284
1	30.08	5.101	857.7649	0.185615	0.906694	5.35008	9.7278
1	30.08	6.209	936.9501	0.184605	0.90176	5.35008	9.7268
1	30.08	7.176	994.4736	0.181965	0.888864	5.35008	9.7241
1	30.08	8.112	1070.528	0.178365	0.871279	5.35008	9.7205
1	30.08	9.157	1146.58	0.177605	0.867566	5.35008	9.7198
1	30.08	10.093	1204.173	0.173445	0.847246	5.35008	9.7156
1	30.08	12.121	1353.534	0.167535	0.818376	5.35008	9.7097
1	30.08	14.149	1499.899	0.161735	0.790044	5.35008	9.7039
1	30.08	16.099	1624.979	0.159235	0.777832	5.35008	9.7014
1	30.08	18.143	1766.68	0.155425	0.759221	5.35008	9.6976
1	30.08	20.155	1887.783	0.156365	0.763813	5.35008	9.6985
1	30.08	22.183	2023.765	0.142645	0.696793	5.35008	9.6848
1	30.08	24.102	2141.134	0.133165	0.650485	5.35008	9.6753
1	30.08	26.13	2269.369	0.128095	0.625719	5.35008	9.6703
1	30.08	28.111	2379.019	0.125325	0.612188	5.35008	9.6675
1	30.08	30.139	2497.892	0.120485	0.588546	5.35008	9.6627
1	30.08	32.23	2612.666	0.115965	0.566467	5.35008	9.6581
1	30.08	34.117	2706.533	0.112675	0.550396	5.35008	9.6549
1	30.08	36.145	2809.705	0.103235	0.504283	5.35008	9.6454
1	30.08	38.111	2892.497	0.099905	0.488016	5.35008	9.6421
1	30.08	40.139	2981.624	0.097745	0.477465	5.35008	9.6399
1	30.08	42.229	3063.227	0.100255	0.489726	5.35008	9.6424
1	30.08	44.273	3129.169	0.099085	0.484011	5.35008	9.6413
1	30.08						
1	30.08	6047.004	3920.822	0.162115	0.791901	5.26448	9.7899
1	30.08	6107.174	3920.87	0.162115	0.791901	5.26448	9.7899
1	30.08	6167.297	3920.875	0.162095	0.791803	5.26448	9.7899
1	30.08	6227.388	3920.961	0.162095	0.791803	5.26448	9.7899
1	30.08	6287.464	3920.971	0.162095	0.791803	5.26448	9.7899
1	30.08	6347.478	3921.097	0.162105	0.791852	5.26446	9.7899

Table F1. Experimental uptake at 30°C (continued).

Step	Tads	Time (sec)	P (kPa)	Uptake (g)	Uptake (g/g)	ZP g)	MP1-ZP (g)
2	30.01	0.219	4078.475	0.200691	0.980339	5.26456	9.79033
2	30.01	1.123	4033.632	0.200691	0.980339	5.26456	9.79033
2	30.01	2.106	4066.295	0.193961	0.947464	5.26456	9.7836
2	30.01	3.105	4100.614	0.184681	0.902133	5.26456	9.77432
2	30.01	4.119	4128.435	0.177251	0.865839	5.26456	9.76689
2	30.01	5.117	4153.008	0.170251	0.831645	5.26456	9.75989
2	30.01	6.24	4174.952	0.164391	0.80302	5.26456	9.75403
2	30.01	7.13	4190.642	0.162331	0.792958	5.26456	9.75197
2	30.01	8.112	4209.622	0.159941	0.781283	5.26456	9.74958
2	30.01	9.126	4226.463	0.156601	0.764968	5.26456	9.74624
2	30.01	10.14	4242.374	0.155301	0.758617	5.26456	9.74494
2	30.01	12.168	4266.187	0.149941	0.732435	5.26456	9.73958
2	30.01	14.212	4288.052	0.148401	0.724912	5.26456	9.73804
2	30.01	16.256	4304.764	0.146781	0.716999	5.26456	9.73642
2	30.01	18.143	4315.866	0.145571	0.711088	5.26456	9.73521
2	30.01	20.171	4324.065	0.145161	0.709085	5.26456	9.7348
2	30.01	22.121	4330.986	0.144471	0.705715	5.26456	9.73411
2	30.01	24.243	4335.983	0.147491	0.720467	5.26456	9.73713
2	30.01	26.115	4339.374	0.147021	0.718171	5.26456	9.73666
2	30.01	28.096	4342.051	0.147741	0.721688	5.26456	9.73738
2	30.01	30.202	4344.633	0.150451	0.734926	5.26456	9.74009
2	30.01	32.183	4346.903	0.150611	0.735708	5.26456	9.74025
2	30.01	34.102	4348.593	0.150781	0.736538	5.26456	9.74042
2	30.01	36.146	4350.276	0.150731	0.736294	5.26456	9.74037
2	30.01	38.267	4351.762	0.152201	0.743474	5.26456	9.74184
2	30.01	40.124	4352.953	0.152311	0.744012	5.26456	9.74195
2	30.01	42.167	4353.977	0.152541	0.745135	5.26456	9.74218
2	30.01	44.102	4355.115	0.152661	0.745722	5.26456	9.7423
2	30.01	46.13	4355.992	0.153121	0.747969	5.26456	9.74276
2	30.01	48.298	4357.14	0.153971	0.752121	5.26456	9.74361
2	30.01	50.139	4357.835	0.154191	0.753195	5.26456	9.74383
2	30.01	52.136	4358.673	0.154381	0.754123	5.26456	9.74402
2	30.01	54.289	4359.449	0.154711	0.755735	5.26456	9.74435
2	30.01						
2	30.01	6587.486	4446.717	0.167711	0.819238	5.24817	9.77374
2	30.01	6647.562	4446.673	0.167751	0.819433	5.24815	9.7738
2	30.01	6707.7	4446.725	0.167721	0.819287	5.24815	9.77377
2	30.01	6767.745	4446.819	0.167701	0.819189	5.24815	9.77375
2	30.01	6827.758	4446.721	0.167701	0.819189	5.24815	9.77375
2	30.01	6887.881	4446.718	0.167711	0.819238	5.24815	9.77376