

**STUDIES ON
GREEN ADSORBENTS AND OPTIMIZATION STRATEGIES
FOR ADSORPTION REFRIGERATION SYSTEM**

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**Studies on
Green Adsorbents and Optimization Strategies
for Adsorption Refrigeration System**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy
to the



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DEDICATED
TO
MY BELOVED PARENTS

DECLARATION

I hereby declare that the work presented here in the thesis entitled “Studies on Green Adsorbents and Optimization Strategies for Adsorption Refrigeration System” has been carried out by me towards the partial fulfilment of the requirement for the award of the degree of Doctor of Philosophy at the Department of Energy Science and Engineering, Indian Institute of Technology Delhi. The content of this thesis, in full or in parts, has not been submitted to any other Institute or University for the award of any degree or diploma by me.

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CERTIFICATE

This is to certify that the thesis entitled “**Studies on Green Adsorbents and Optimization Strategies for Adsorption Refrigeration System**” being submitted by **Mr. Prathvi Raj Chauhan** in fulfilment of the requirements for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work performed by him under my guidance and supervision at **Department of Energy Science and Engineering, Indian Institute of Technology Delhi**.

Further, the results obtained herein have not been submitted in part or in full to any other University or Institute for the award of any degree to the best of my knowledge.

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(Prathvi Raj Chauhan)

ABSTRACT

The global energy demand, particularly for cooling, refrigeration, and air-conditioning, has been rising rapidly, correlating with the standard of living, which is also responsible for a high amount of greenhouse gases (GHGs) harming the environment and climate change. Thus, there is a need for effective utilization of waste thermal energy including renewable fuels and resources to reduce escalating energy demand, thereby mitigating the climate change. The cooling requirements for refrigeration and air-conditioning contribute significantly to global energy consumption, expected to triple by the mid of this century. Approximately 17% of global electricity is consumed by conventional cooling and heating systems, primarily reliant on fossil fuels, leading to resource depletion and greenhouse gas emissions. Moreover, many remote areas face challenges due to electricity scarcity, posing challenges for conventional refrigeration and air-conditioning for critical applications like food storage and preservation of life-saving drugs. The depletion of fossil fuels, environmental concerns, and challenges in remote areas intensify the urgency to develop sustainable technologies, drawing attention to ecological and renewable energy resources.

In countries like India, surplus biomass is often burnt *in-situ*, contributing to resource wastage, air pollution, and environmental degradation. Converting crop residues into value-added products could serve as a mitigation strategy against biomass wastage and *in-situ* burning. Alongside improving energy efficiency and biomass waste management, alternative heat-powered cooling technologies are essential to reduce grid dependency for refrigeration and air-conditioning. The adsorption technology has emerged as the promising solution, operating on low-temperature heat sources like Solar thermal, geothermal energy, and biomass combustion heat, and ensuring lower maintenance due to fewer moving parts. However, challenges such as bulky systems and high operating costs have hindered the commercialization of adsorption technology. Despite these setbacks, advancements in adsorber

designs, novel adsorbents, multi-stage schemes, heat and mass recovery schemes, and control mechanisms offer avenues for enhancement. This thesis contributes to advancing adsorption refrigeration systems through experimental and numerical studies, aiming to optimize parameters, improve efficiency, and pave the way for a more sustainable and commercially viable cooling technology.

An extensive literature survey highlights a huge variation in the thermal performance of adsorption refrigeration systems with different porous materials. Therefore, a thermal performance estimation of a single-stage vapour adsorption system using various carbon-based adsorbents with ethanol refrigerant has been studied. The system is coupled with a small-scale biomass-based heating unit for space cooling, refrigeration, and heat pumping applications. The detailed investigation explored the impacts of operating parameters, and heat exchanger to adsorbent mass ratio on specific cooling energy (SCE), coefficient of performance (COP), uptake efficiency (η_u), and mass of adsorbent to combustion fuel to identify the suitable adsorbent and sorption bed designs for each application. One of the promising biomass-based adsorbents with finned flat-tube adsorbers outperforms traditional designs by 19-30%. Further, biomass-based adsorbents not only demonstrate superior performance, with higher COPs and efficiency for heat-pumping applications, but also require the least amount of adsorbent to achieve the desired effect per unit mass of combustion fuel in biomass heating units.

The thermal performance enhancement of an advanced adsorption chiller involves a comprehensive assessment focusing on entropy generation minimization through appropriate operating strategies, temperatures, and design modifications. The analysis involved a second law evaluation of a two-bed silica gel water pair-based adsorption cooling system, exploring novel aspects like heat recovery and measures to reduce auxiliary consumption. The specific irreversibility index, reflecting entropy generation, auxiliary electricity consumption, and cooling capacity, serves as an indicator for second law efficiency. The numerical evaluation

shows around 63% reduction in entropy generation with a passive heat recovery strategy, and up to 22% decrease in specific irreversibility with a capillary-assisted evaporator. Additionally, a multi-objective optimization is conducted considering wetness fraction and hot flushing effects, employing the NSGA II and LINMAP techniques. The research findings highlight the substantial contributions of precooling, preheating, and flushing processes to exergy destruction, emphasizing the importance of a heat recovery scheme. The proposed optimized values of COP and specific exergy destruction (e_D) under passive heat recovery indicate improvements of +18.56% and -27.63%, respectively, compared to a system without heat recovery.

The crop residue management in India, marked by the longstanding issue of *in-situ* burning causing climate change, health concerns, and soil degradation, is a critical challenge. Simultaneously, adsorption refrigeration faces obstacles in commercialization due to bulkiness and inadequate performance linked to unsuitable adsorbents. To address both concerns, the present study focused on green synthesis, detailed characterization, and sustainable application of porous activated carbons derived from abundant crop residues. The optimized biochar, activated with KOH, exhibits substantial surface areas of 2002 m²/g for sugarcane bagasse (SBAC) and 1241 m²/g for rice straw (RSAC), surpassing commercial activated carbons. These novel activated carbons exhibit superior performance, notably in ethanol uptake, making them promising candidates for efficient and sustainable cooling and heat-pumping applications in renewable energy-powered systems. The proposed SBAC-ethanol pair demonstrates higher effective uptake and energy density compared to similar adsorbents, showcasing the potential of synthesized activated carbons. This research recommends the proposed activated carbons as promising candidates for efficient and sustainable cooling and heat-pumping applications, offering a potential solution to both crop residue management challenges and the enhancement of adsorption refrigeration technology.

वैश्विक ऊर्जा मांग, विशेष रूप से शीतलन, प्रशीतन और वातानुकूलन के लिए, तेजी से बढ़ रही है, जो जीवन स्तर से संबंधित है, जो पर्यावरण और जलवायु परिवर्तन को नुकसान पहुंचाने वाली ग्रीनहाउस गैसों (जीएचजी) की उच्च मात्रा के लिए भी जिम्मेदार है। इस प्रकार, ऊर्जा की बढ़ती मांग को कम करने के लिए नवीकरणीय ईंधन और संसाधनों सहित अपशिष्ट तापीय ऊर्जा के प्रभावी उपयोग की आवश्यकता है, जिससे जलवायु परिवर्तन को कम किया जा सके। प्रशीतन और वातानुकूलन के लिए शीतलन आवश्यकताएँ वैश्विक ऊर्जा खपत में महत्वपूर्ण योगदान देती हैं, जो इस सदी के मध्य तक तीन गुना होने की उम्मीद है। वैश्विक बिजली का लगभग 17% पारंपरिक शीतलन और तापक प्रणाली द्वारा खपत किया जाता है, जो मुख्य रूप से जीवाश्म ईंधन पर निर्भर है, जिससे संसाधन में कमी और ग्रीनहाउस गैस उत्सर्जन होता है। इसके अलावा, कई दूरदराज के इलाकों को बिजली की कमी के कारण चुनौतियों का सामना करना पड़ता है, जिससे खाद्य भंडारण और जीवन रक्षक दवाओं के संरक्षण जैसे महत्वपूर्ण अनुप्रयोगों के लिए पारंपरिक प्रशीतन और वातानुकूलन के लिए चुनौतियाँ पैदा होती हैं। जीवाश्म ईंधन की कमी, पर्यावरणीय चिंताएँ और दूरदराज के क्षेत्रों में चुनौतियाँ टिकाऊ प्रौद्योगिकियों को विकसित करने की आवश्यकता को बढ़ाती हैं, जिससे पारिस्थितिक और नवीकरणीय ऊर्जा संसाधनों की ओर ध्यान आकर्षित होता है।

भारत जैसे देशों में, अधिशेष बायोमास को अक्सर वहीं जला दिया जाता है, जो संसाधनों की बर्बादी, वायु प्रदूषण और पर्यावरणीय गिरावट में योगदान देता है। फसल अवशेषों को मूल्यवर्धित उत्पादों में परिवर्तित करना बायोमास बर्बादी और यथास्थान जलाने के खिलाफ शमन रणनीति के रूप में काम कर सकता है। ऊर्जा दक्षता और बायोमास अपशिष्ट प्रबंधन में सुधार के साथ-साथ, प्रशीतन और वातानुकूलन के लिए ग्रिड निर्भरता को कम करने के लिए वैकल्पिक ताप-संचालित शीतलन प्रौद्योगिकियाँ आवश्यक हैं। सोखना तकनीक आशाजनक समाधान के रूप में उभरी है, जो सौर तापीय, भू-तापीय ऊर्जा और

बायोमास दहन ताप जैसे कम तापमान वाले ताप स्रोतों पर काम करती है, और कम चलने वाले हिस्सों के कारण कम रखरखाव सुनिश्चित करती है। हालाँकि, भारी निकाय और उच्च परिचालन लागत जैसी चुनौतियों ने सोखना प्रौद्योगिकी के व्यावसायीकरण में बाधा उत्पन्न की है। इन असफलताओं के बावजूद, अधिशोषक रचना, नवीन अधिशोषक, मल्टी-स्टेज योजनाएं, ताप और द्रव्यमान पुनर्प्राप्ति योजनाएं और नियंत्रण तंत्र में प्रगति वृद्धि के रास्ते प्रदान करती है। यह शोध प्रबंध प्रायोगिक और संख्यात्मक अध्ययनों के माध्यम से सोखना प्रशीतन प्रणालियों को आगे बढ़ाने में योगदान देती है, जिसका लक्ष्य मापदंडों को अनुकूलित करना, दक्षता में सुधार करना और अधिक टिकाऊ और व्यावसायिक रूप से व्यवहार्य शीतलन तकनीक का मार्ग प्रशस्त करना है।

एक व्यापक साहित्य सर्वेक्षण विभिन्न छिद्रयुक्त सामग्रियों के साथ सोखने वाले प्रशीतन प्रणालियों के उष्णता प्रदर्शन में भारी भिन्नता पर प्रकाश डालता है। इसलिए, इथेनॉल रेफ्रिजरेंट के साथ विभिन्न कार्बन-आधारित अवशोषक का उपयोग करके एकल-चरण वाष्प सोखना प्रणाली के उष्णता प्रदर्शन अनुमान का अध्ययन किया गया है। प्रणाली को स्थान शीतलन, प्रशीतन और ताप पंपिंग अनुप्रयोगों के लिए एक छोटे पैमाने पर बायोमास-आधारित तापन इकाई के साथ जोड़ा गया है। विस्तृत जांच हेतु संचालन मापदंडों और हीट एक्सचेंजर से सोखना पदार्थ द्रव्यमान अनुपात के प्रभावों का विशिष्ट ठंडा ऊर्जा (एससीई), प्रदर्शन का गुणांक (सीओपी), उपभोग दक्षता (η_u), और दहन ईंधन के लिए सोखना पदार्थ द्रव्यमान पर अध्ययन किया गया है ताकि प्रत्येक अनुप्रयोग के लिए उपयुक्त सोखना पदार्थों और सोखने तल रचनाओं की पहचान की जा सके। पंखयुक्त फ्लैट-ट्यूब अवशोषक के साथ एक आशाजनक बायोमास-आधारित अवशोषक पारंपरिक रचना से 19-30% बेहतर प्रदर्शन करता है। इसके अलावा, बायोमास आधारित अधिशोषक पदार्थों ने न केवल गर्मी पंपिंग अनुप्रयोगों के लिए उच्चतर सीओपी और दक्षता के साथ उत्कृष्ट प्रदर्शन दिखाया, बल्कि बायोमास तापन इकाई में दहन ईंधन के प्रति यूनिट द्रव्यमान में वांछित प्रभाव प्राप्त करने के लिए कम से कम मात्रा में अधिशोषक की भी आवश्यकता होती है।

एक उन्नत सोखना चिलर के थर्मल प्रदर्शन को बढ़ाने में उचित संचालन रणनीतियों, तापमान और डिजाइन संशोधनों के माध्यम से एन्ट्रापी उत्पादन को कम करने पर ध्यान केंद्रित करने वाला एक व्यापक मूल्यांकन शामिल है। विश्लेषण में दो-बेड सिलिका जेल एवं जल जोड़ी-आधारित सोखना शीतलन प्रणाली का ऊष्मागतिकी का दूसरा नियम शामिल है, जिसमें गर्मी पुनर्प्राप्ति और सहायक खपत को कम करने के उपायों जैसे नए पहलुओं का पता लगाया गया है। विशिष्ट अपरिवर्तनीयता सूचकांक, जो एंट्रॉपी उत्पादन, सहायक बिजली खपत, और ठंडा क्षमता को दर्शाता है, ऊष्मागतिकी का दूसरा नियम दक्षता के लिए एक संकेतक के रूप में कार्य करता है। संख्यात्मक मूल्यांकन निष्क्रिय ताप पुनर्प्राप्ति रणनीति के साथ एन्ट्रापी उत्पादन में लगभग 63% की कमी दिखाता है, और केशिका-सहायता वाले बाष्पीकरणकर्ता के साथ विशिष्ट अपरिवर्तनीयता में 22% तक की कमी दिखाता है। इसके अतिरिक्त, एनएसजीए ॥ और लिनमैप तकनीकों को नियोजित करते हुए, गीलेपन अंश और गर्म फ्लशिंग प्रभावों पर विचार करते हुए एक बहुउद्देश्यीय अनुकूलन आयोजित किया जाता है। शोध के निष्कर्ष गर्मी वसूली योजना के महत्व पर जोर देते हुए, ऊर्जा विनाश में प्रीकूलिंग, प्रीहीटिंग और फ्लशिंग प्रक्रियाओं के महत्वपूर्ण योगदान को उजागर करते हैं। निष्क्रिय ताप पुनर्प्राप्ति के तहत सीओपी और विशिष्ट ऊर्जा विनाश (e_D) के प्रस्तावित अनुकूलित मूल्य, ताप पुनर्प्राप्ति के बिना प्रणाली की तुलना में क्रमशः +18.56% और -27.63% के सुधार का संकेत देते हैं।

भारत में फसल अवशेष प्रबंधन, जो लंबे समय से स्थल पर जलाने की समस्या से जुड़ा हुआ है, जिससे जलवायु परिवर्तन, स्वास्थ्य संबंधी चिंताएँ और मृदा क्षरण होता है, एक गंभीर चुनौती है। इसके साथ ही, अनुपयुक्त अधिशोषक से जुड़े भारीपन और अपर्याप्त प्रदर्शन के कारण अधिशोषण प्रशीतन को व्यावसायीकरण में बाधाओं का सामना करना पड़ता है। दोनों चिंताओं को दूर करने के लिए, वर्तमान अध्ययन हरित संश्लेषण, विस्तृत लक्षण वर्णन और प्रचुर फसल अवशेषों से प्राप्त छिद्रयुक्त सक्रिय कार्बन के टिकाऊ अनुप्रयोग पर केंद्रित है। KOH के साथ सक्रियित किया गया अनुकूलित बायोचार, गन्ने की खोई (एसबीएसी) के लिए 2002 m^2/g और पराली (आरएसएसी) के लिए 1241 m^2/g के पर्याप्त सतह

क्षेत्रों को प्रदर्शित करता है, जो वाणिज्यिक सक्रिय कार्बनों से बेहतर है। ये नए सक्रिय कार्बन विशेष रूप से इथेनॉल ग्रहण में उत्कृष्ट प्रदर्शन करते हैं, जो उन्हें नवीकरणीय ऊर्जा-संचालित प्रणालियों में कुशल और टिकाऊ शीतलन और ताप-पंपिंग अनुप्रयोगों के लिए आशाजनक उम्मीदवार बनाते हैं। प्रस्तावित एसबीएसी-इथेनॉल जोड़ी समान अधिशोषक की तुलना में उच्च प्रभावी ग्रहण और ऊर्जा घनत्व प्रदर्शित करती है, जो संश्लेषित सक्रिय कार्बन की क्षमता को प्रदर्शित करती है। यह शोध प्रस्तावित सक्रिय कार्बन को कुशल और स्थायी शीतलन और ताप-पंपिंग अनुप्रयोगों के लिए आशाजनक उम्मीदवारों के रूप में अनुशासित करता है, जो फसल अवशेष प्रबंधन चुनौतियों और सोखना प्रशीतन प्रौद्योगिकी के संवर्धन के लिए एक संभावित समाधान प्रदान करते हैं।

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NOMENCLATURE

a	Area of cross-section of mass transfer, (m^2)
A, B, C	Antoine equation coefficients, (-)
c_p	Specific heat, ($kJ/kg \cdot K$)
d	Heterogeneity parameter, (-) or diameter, (mm)
D_0	Preexponential constant, (m^2/s)
d_p	Average pore width, (nm)
E or E_a	Activation energy, (kJ/kg)
\dot{E}_D	Exergy destruction rate, (kW/kg)
e_D	Specific exergy destruction, (kJ/kJ)
h	Height, (mm)
HCV	Higher calorific value, ($kcal/kg$)
h_{fg}	Latent heat of vaporization, (kJ/kg)
k	Thermal conductivity, ($W/m \cdot K$)
K_0	Pre exponential Toth's constant, (Pa^{-1})
LHV	Lower heating value, ($kcal/kg$)
m or M	Mass, (kg)
\dot{m}	Mass flow rate, (kg/s)
n	Index parameter, (-)
N	Number of segments
P	Pressure, (kPa)
P_{eq}	Equilibrium pressure, (kPa)
P_r	Relative pressure, (kPa/kPa)
P_s	Saturation pressure, (kPa)
Q	Thermal energy, (kJ)
Q_{st}	Isosteric heat of adsorption, (kJ/kg)
\dot{Q}	Heat transfer rate, (kW)
R	Gas constant, ($kJ/kg \cdot K$)
R_p	Radius of adsorbent particle, (m)
S	Surface area, (m^2/g)
SCE	Specific cooling energy, (kJ/kg)
\dot{S}_{gen}	Entropy generation rate, ($kW/kg \cdot K$)
T	Temperature, (K)

t	Time, (s)
T_0	Reference or dead state temperature, (K)
UA	Overall heat transfer capability (kW/K)
V	Volume, (m ³)
V_a	Volume of gas adsorbed, (cm ³ /g)
V_p	Micropore volume, (cm ³ /g)
W or x_{eq}	Equilibrium adsorption uptake, (kg/kg)
W_o	Maximum adsorption uptake, (kg/kg)
x	Concentration of refrigerant, (kg/kg)
x^*	Saturation concentration of refrigerant, (kg/kg)

Greek symbols

α	Correlation coefficients
β	Constant
Δ	Difference
η	Efficiency
θ	Surface coverage
ρ	Density, (kg/m ³)
φ	Time of commencement of switchover phase, (s)

Abbreviations

AC	Activated carbon
ACDS	Adsorption cooling cum desalination system
ACF	Activated carbon fibre
ACS	Adsorption cooling system
BET	Brunauer-Emmett-Teller
BP	British Petroleum
CAC	Commercial activated carbon
CC	Cooling capacity
COF	Covalent organic framework
COP	Coefficient of performance
CP	Cooling power
DI	Deionised water

DSC	Differential scanning calorimetry
ED	Exergy destruction rate
FESEM	Field emission scanning electron microscopy
FFT	Flat finned tube
FTIR	Fourier transform infrared
GA	Genetic algorithm
GNP	Graphene nanoplatelet
HEx	Heat exchanger
HMR	Heat and mass recovery
HR	Heat recovery
HS	Hybrid system
HT	Heat transfer
LINMAP	Linear programming technique for multidimensional analysis of preference
LMTD	Logarithmic temperature difference
M	Mangrove wood
MOF	Metal-organic framework
MR	Mass recovery
MXC or ACC	MaxorbIII composite
N	Number of pores
NLDFT	Non-local density functional theory
NRMSE	Normalized root mean square error
NSGA	Non-dominated sorting genetic algorithm
PSO	Particle swarm optimization
PVA	Polyvinyl alcohol
RS	Rice straw
RSAC	Rice straw-derived activated carbon
SB	Sugarcane bagasse
SBAC	Sugarcane bagasse-derived activated carbon
SCP	Specific cooling power
SDWP	Specific daily water production
T&S	Tube and shell
TCE	Thermal conductivity enhancer
TFT	Traditional finned tube

WP	Working pair
WPT	Waste palm trunk
XRD	X-Ray diffraction

Sub- and Super- scripts

act	Actual or activation
ad	Adsorbent
ads	Adsorption
adsr	Adsorber
amb	Ambient
appx	Approximately
avg	Average
bed	Adsorbent bed
carbo	Carbonization
Cdev	Combustion device or gasifier
cf	Combustion fuel
chill	Chilled water
comb	Combustion
cond	Condenser
cool or c	Cooling or adsorption
coolT	Cooling tower
cyc	Cycle
des	Desorption
desr	Desorber
eff	Effective
eq	Equilibrium
evap	Evaporator
exe	Exergy
exp	Experimental
f	Final
HEX	Heat exchanger
hot or h	Heating or desorption
hotF	Hot flushing
hp	Heat pumping

HR	Heat recovery
Hrej	Heat rejection
HT	Heat transfer
i	Initial or inner
in	Inlet or input
max	Maximum
meso	Mesopores
micro	Micropores
min	Minimum
MR	Mass recovery
MT	Mass transfer
norm	Normalized
num	Numerical
opt	Optimum
out	Outlet
p	Particle
pore	Pores
preC	Precooling
preH	Preheating
rec	Recovery
ref	Refrigerant
short	Shortest
switch	Switching
thermC	Thermal compression
thermS	Thermal energy source
tot	Total
u	Uptake
void	Voids in adsorbent
w	Water