HYDROTHERMAL CONVERSION OF BIOMASS TO BIOFUEL AND ITS CATALYTIC UPGRADATION

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HYDROTHERMAL CONVERSION OF BIOMASS TO BIOFUEL AND ITS CATALYTIC UPGRADATION

by

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Department of Chemical Engineering

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Dedicated to

Mango & Apple

‘My lovely nieces’

CERTIFICATE

This is to certify that the thesis entitled, **"HYDROTHERMAL CONVERSION OF BIOMASS TO BIOFUEL AND ITS CATALYTIC UPGRADATION"** submitted by '**Mr. Dinesh Kumar'** to the **Indian Institute of Technology Delhi** for the award of Degree of **Doctor of Philosophy** is a record of original bonafide research work carried out by him under my guidance and supervision. The thesis has reached the standards of fulfilling the requirements of the regulations of Indian Institute of Technology Delhi for awarding the degree.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

New Delhi

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ABSTRACT

Conversion of *Pongamia pinnata, Jatropha curcasa* and Tung de-oiled seed cake to biocrude was investigated. Prior to conversion studies, detailed physicochemical characterizations of seed cakes were performed by proximate analysis, ultimate analysis, HHV analysis, SEM, TGA, lignocellulosic content analysis, XRD, FT-IR. The conversion of seed cakes was investigated using pyrolysis (Temperature: 400-600^{o}C), steam pyrolysis (Steam rate: 1-5 cm/sec) and hydrothermal conversion (Pressure: 10-50 kg/cm^2) processes. Biocrude obtained was characterized using GC/MS, TGA, CHNO, FT-IR, GC, TAN, density, calorific value, viscosity and silica adsorption chromatography. *Pongammia* cake conversion using hydrothermal process was considered for further investigations due to its maximum conversion to biocrude yield (35.3% ± 1.3%).

Response surface methodology coupled with centre composite design was used for generating quadratic model equations for maximizing biocrude yield and hydrocarbon fraction in the range of boiling range of C_6-C_{24} straight chain alkanes. Result revealed that temperature and time were the individual significant parameters for biocrude yield whereas pressure was the only individual significant parameter on the C_6-C_{24} hydrocarbon fraction. Errors between experimentally obtained and predicted values were -12.5% to +11.1% for biocrude yield and 8.5% to -7.5% for C_6-C_{24} hydrocarbons fraction. Optimized process parameters for the maximum biocrude yield coupled with C_6-C_{24} hydrocarbons fraction were obtained as T= 400°C (temperature), P= 25 kg/cm^2 (pressure), t= 35 minutes (reaction time) and W/B ratio = 2.

Biocrude obtained after the thermochemical conversion has high content of heavy hydrocarbons as well as oxygen content, which creates instability issues. To reduce the viscosity, corrosiveness and stability issue, biocrude upgradation studies were conducted using various

methods. The studies were accomplished using three methods available in literature (i) addition of hydrogen donor solvent, (ii) cracking in presence of alkali/alkaline earth metal catalysts in different forms, and (iii) using heteroatom impregnated mesoporous catalyst.

A decrease in the biocrude yield was observed from 35.3% to 32.1%, 31.1% and 27.6% in presence of tetraline, ethanol and acetone respectively. Maximum yield of biocrude (28.2%) was obtained in the presence of KCl as compared to all other catalysts. In presence of alkali a sharp increase in the gaseous products was also observed.

The upgradation studies were conducted in presence of siliceous and aluminated mesoporous catalysts e.g. FDU-12, SBA-15 and KIT-6 having large pores. All the catalysts were characterized using SEM, N_2 adsorption-desorption, NH_3-TPD and TPR, BJH, FTIR, ICP, XRD etc. SBA-15 with SAR 30 was considered for detailed studies due to maximum biocrude yield (~33.5%). GC analysis showed an increase of C_{11}-C_{18} range hydrocarbons (based on boiling point) from 16.3% to 23.7% over Al/SBA-15. Further the optimization of SAR was conducted from 20 to 50 over SBA-15. GC/MS analysis confirmed Al/SBA-15 with SAR 40 as a promising catalyst for maximum increase of hydrocarbons (Aliphatics and benzene type). Three noble metals Pd, Ga and Ru, with 3% (by weight) loading over Al/SBA-15 having SAR 40, were tested for reducing the oxygen content of the biocrude. The performance of 3%Pd/AlSBA-15(SAR 40) was found most suitable in terms of lowest TAN (~20.5 mg KOH/g biocrude), maximum calorific value (~38.4 MJ/kg) and minimum oxygenated compound fraction (~25.5%) as compared to Ga and Ru loaded catalyst.

Further for evaluation of activation energy and rate constant, experiments were conducted between 325-425^{o}C & 20-30 kg/cm^2. Six lump model which includes one gaseous phase lump,

one solid phase lump and four lumps from liquid phase were generated. Kinetic parameters were evaluated using MATLAB and Marquardt's method considering a combination of 1^{st} and 2^{nd} order kinetics. Estimated activation energy for different lumps were between 9.8 KJ/mol to 33.2 KJ/mol much below than the value available for pyrolysis studies (80-300 KJ/mol). Errors were estimated for each lump and were found from 11% (for lower boiling range hydrocarbons) to 30% for char and gaseous fraction.

TABLE OF CONTENTS

		Page No.
Certificate		i
Acknowledgments		ii
Abstract		v
Table of Contents		viii
List of Figure		xii
List of Tables		xix
Nomenclature		xxiii
CHAPTER 1: INTRODUCTION		1
1.1	Background	1
1.2	Motivation of study	7
1.3	Objectives of the work	8
1.4	Thesis organization	9
CHAPTER 2: LITERATURE REVIEW		11
2.1	Energy scenario	11
	2.1.1 Indian context	12
2.2	Biomass	14
	2.2.1 Biomass composition	15
	2.2.2 Conversion routes of biomass to liquid biofuel	22
	2.2.2.1 Pyrolysis	22
	2.2.2.2 Hydrothermal conversion	23
	2.2.2.3 Elementary steps in thermal hydrocarbon chemistry	26
2.3	Conversion of biomass to biocrude: literature review	26
	2.3.1 Pyrolysis	26
	2.3.2 Hydrothermal/Liquefaction conversion	33
	2.3.3 Optimization of process parameters	36
2.4	Upgrading of biocrude	39
	2.4.1 Insitu upgradation using alkali/alkaline earth metal	42

2.4.2 Insitu upgradation using solvolysis 46
2.4.3 Upgradation of biocrude using heterogeneous catalyst 50
2.4.3.1 Mechanism of mesoporous catalyst synthesis 52
2.4.3.2 Mesoporous catalysts in biorefinery 53
2.4.3.3 Use of transition metals for cracking reaction 59
2.4.3.4 Use of transition metals for de-oxygenations reactions 61
2.5 Lump kinetic modeling for estimation of kinetic parameters 63
2.6 Gaps identified from the literature 69

CHAPTER 3: EXPERIMENTAL DETAILS 70
3.1. Raw material 70
3.2. Catalyst synthesis 70
3.2.1 Synthesis of SBA-15 71
3.2.2 Synthesis of FDU-12 71
3.2.3 Synthesis of KIT-6 71
3.2.4 Direct synthesis of aluminated catalyst 72
3.2.5 Synthesis of noble metal loaded aluminated catalyst 72
3.3 Catalytic activity tests for pyrolysis and hydrothermal conversion 73
3.4 Characterization and analysis 76
3.4.1 Characterization of seed cake and biochar 76
3.4.2 Catalyst characterization 78
3.4.2.1 BET surface area and pore volume measurement 78
3.4.2.2 Temperature Programmed Reduction and H_2- pulse chemisorptions 79
3.4.2.3 X-ray Diffraction 80
3.4.2.4 Fourier Transform Infrared Spectroscopy 81
3.4.2.5 Thermogravimetric Analysis 81
3.4.2.6 Scanning Electron Microscope 82
3.4.3 Product analysis 82
3.4.4 Important definitions 85

3.5 Design of experiments 86
3.5.1 Plackett-Burman design 86
3.5.2 Design of experiments for developing quadratic model 86

CHAPTER 4: SELECTION OF NON-EDIBLE OIL SEED CAKE AND THERMOCHEMICAL PROCESS FOR BIOCRUDE PRODUCTION 88
4.1 Characterization of seed cake 88
4.2 Thermochemical conversion of seed cake to biocrude 92
4.3 Product characterization 97
4.3.1 Biocrude characterization and analysis 97
4.3.2 Biochar characterization 108
4.3.3 Gaseous product analysis 112

CHAPTER 5: PROCESS PARAMETER OPTIMIZATION for HYDROTHERMAL CONVERSION of *Pongamia* CAKE to PRODUCE BIOCRUDE 115
5.1 Preliminary screening of process parameter 115
5.2 Model development using DOE 117
5.2.1 Individual and combined effect of process parameters 122
5.3 Optimization of parameters 131

CHAPTER 6: BIOCRUDE UPGRADATION 135
6.1 Solvent effect on the biocrude yield and quality 135
6.2 Effect of akali/alkaline earth metals in various forms as catalyst (carbonates, hydroxide and chloride) on biocrude yield 139
6.3 Catalytic insitu upgradation 143
6.3.1 Characterization of catalyst 143
6.3.2 Catalytic activity tests over siliceous and aluminated mesoporous catalyst 149
6.3.2.1 Biocrude analysis 153
6.3.3 Optimization of alumina loading on SBA-15 for improving 160

biocrude yield
6.3.4 Effect of noble metal loading on deoxygenation of biocrude 165

CHAPTER 7: LUMP MODELING for PRODUCTION of BIOFUEL from *Pongamia* CAKE via HYDROTHERMAL CONVERSION 175
7.1 Design of kinetic experiments and lump kinetic modeling 175
7.2 Kinetics studies 176
7.2.1 Effect of temperature on different lump yields 176
7.2.2 Effect of pressure on the middle distillate range hydrocarbon 178
7.3 Deplots analysis 179
7.4 Estimation of kinetic parameters 182
7.5 Goodness of Fit 189

CHAPTER 8: CONCLUSIONS AND SCOPE OF FUTURE WORK 195
8.1 Conclusions 195
8.2 Scope of future work 200

REFERENCES 201

APPENDICES 230

AUTHOR BIO-DATA 242

LIST OF FIGURES

Figure No.	Title	Page No.
1.1	Estimated trend of various energy resources consumption between 1990 and 2040.	1
1.2	Growth in global energy consumption trend for various energy consuming sectors between 1980-2040.	2
1.3	Bio-fuel: A sustainable energy alternative with respect to CO_2 cycle.	4
2.1	Overview of processing of crude feedstock to refined products.	14
2.2	Comparison of biofuel generations.	15
2.3	D glucose units with β (1,4)-glycosidic linkages present in cellulose.	16
2.4	Chemical structure of hemicellulose.	17
2.5	Chemical structure of lignin showing various bonds of three major phenolic constituents	18
2.6	Pyrolytic conversion of biomass to various products	23
2.7	Density, dielectric constant and ion dissociation constant of water as a function of temperature.	24
2.8	Mechanisms for hydrothermal conversion of lignocellulosic biomass.	25
2.9	Packing factor and space group for silica based mesoporous catalyst.	54
3.1	Schematic diagram of the experimental set-up for pyrolysis reactor.	74
3.2	Schematic diagram of the experimental set-up for hydrothermal process.	74
3.3	Procedure for product separation and analysis.	77
4.1	Lignin, cellulose and hemicellulose composition of *Pongamia*, *Jatropha* and Tung seed cake.	89
4.2	FT-IR spectrum of *Jatropha, Pongamia* and Tung seed cake.	90
4.3	XRD patterns of *Jatropha, Pongamia* and Tung seed cake.	91
4.4	Effect of temperature on the biocrude yield during pyrolytic	92

conversion of seed cakes. (t =10 minutes)

4.5 Effect of steam rate on the biocrude yield during steam-pyrolytic conversion of seed cakes (T= 500^oC; t=10 minutes). 93

4.6 Effect of pressure on the biocrude yield during hydrothermal conversion of seed cakes (T= 400^oC; W/B=3; t=40 minutes) 94

4.7 Effect of pressure on hydrocarbon distribution (based on boiling point) during hydrothermal conversion (T= 400^oC; W/B=3; t= 40 minutes). 95

4.8 Yield of different products obtained from hydrothermal conversion (T=400^oC, t=40 minutes; W/B=3; P=30 kg/cm^2) 96

4.9 Energy content of three seed cakes and different biocrudes (at maximum yield) obtained from thermochemical conversion of seed cakes 98

4.10 FT-IR of different biocrudes obtained from hydrothermal conversion of three seed cakes (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B=3) 99

4.11 GC analysis of biocrude obtained from hydrothermal conversion of three seed cakes (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B = 3) 101

4.12 ^{1}H NMR distribution of biocrude obtained from hydrothermal conversion of three seed cakes (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B=3) 102

4.13 Silica adsorption chromatography analysis of *Jatropha* biocrude obtained from thermochemical conversion (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B = 3) 103

4.14 Silica adsorption chromatography analysis of *Pongamia* biocrude obtained from thermochemical conversion. (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B = 3) 103

4.15 Silica adsorption chromatography analysis of Tung biocrude obtained from thermochemical conversion. (T=400^oC P=30 kg/cm^2; t = 40 minutes; W/B = 3) 104

4.16 van-Krevelen diagram of seed cakes and respective biochar obtained from hydrothermal conversion (T=400^oC; P=30 kg/cm^2; t= 40 110

	minutes; W/B=3)	
4.17	TGA analysis of seed cakes and respective biochar obtained from hydrothermal conversion (T=400^oC; P=30 kg/cm^2; t=40 minutes; W/B= 3)	110
4.18	SEM images of biochar obtained after hydrothermal conversion of (a) *Pongamia* (b) *Jatropha* (c) Tung (T=400^oC; P=30 kg/cm^2; t= 40 minutes; W/B=3)	113
5.1	Pareto chart at the absolute values for optimization of process parameter using Plackett–Burman design.	116
5.2 (a)	Box cox plots for the lambda value of the biocrude yield.	123
5.2 (b)	Box cox plots for the lambda value of C_6-C_{24} hydrocarbons fraction.	123
5.3	Effect of individual process parameters on the biocrude yield and C_6-C_{24} hydrocarbon fraction.	124
5.4	Combined effect of temperature with (a, d) pressure, (b, e) time and (c, f) W/B ratio (α=+1 and α=-1) on the biocrude yield and C_6-C_{24} hydrocarbon fraction.	127
5.5	Combined effect of pressure with (a, d) temperature, (b, e) time and (c, f) W/B ratio (at α=+1 and α=-1) on the biocrude yield and C_6-C_{24} hydrocarbon fraction.	128
5.6	Combined effect of time, with (a, d) temperature, (b, e) pressure and (c, f) W/B ratio (at α=+1 and α=-1) on the biocrude yield and C_6-C_{24} hydrocarbon fraction.	130
5.7	Superimposed plots for biocrude yield (black line) and C_6-C_{24} hydrocarbons fraction (blue line) with their respective value at various process parameter conditions.	132
5.8	Comparison between predicted and experimentally obtained values of biocrude yield and C_6-C_{24} hydrocarbons fraction for hydrothermal conversion of *Pongamia* seed cake.	133
6.1	Effect of different solvent and their loading on the biochar yield	136

	(T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; (W+S)/B =2)	
6.2	Effect of different solvent and their loading on the biocrude yield (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; (W+S)/B =2)	136
6.3	Effect of different solvent and their loading on the gas yield (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; (W+S)/B =2)	137
6.4	Effect of different earth metal carbonates on biocrude yield (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10)	140
6.5	Effect of different earth metal hydroxides on biocrude yield (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10)	140
6.6	Effect of different earth metal chlorides on biocrude yield (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10)	141
6.7	Effect of different earth metal on the gas yield at various loading (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10)	142
6.8	N_2 adsorption-desorption curve of calcined SBA-15, KIT-6 and FDU-12.	144
6.9	N_2 adsorption-desorption curve of calcined SBA-15, KIT-6 and FDU-12 with SAR 30.	145
6.10	FT-IR analysis of calcined SBA-15, KIT-6 and FDU-12.	146
6.11	X-Ray Diffraction of as synthesized SBA-15, FDU-12 and KIT-6.	148
6.12	Thermogravemetric analysis of as synthesized SBA-15, FDU-12 and KIT-6.	148
6.13	Scanning Electron Microscopic images of as synthesized, alumina loaded mesoporous materials (a) SBA-15, (b) FDU-12 and (c) KIT-6	150
6.14	Product yield obtained after hydrothermal conversion (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10)	151
6.15	Asphaltene content of various biocrudes obtained after insitu upgradation (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10)	157
6.16	GC/MS analysis of desirable fraction of biocrude obtained after insitu catalytic upgradation (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10)	158

6.17 GC/MS analysis of undesirable fraction of biocrude obtained after insitu catalytic upgradation. (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 158

6.18 Effect of different SAR on hydrocarbon fractions of transportation grade fuel. (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 161

6.19 Effect of varying SAR on various subfrcation present in the bicrude (T=400^{o}C, P=25 kg/cm^2, t= 35 minutes; W/B ratio =2; C/B =1:10). 162

6.20 GC/MS analysis of biocrude obtained in presence of different alumina loaded SBA-15 (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 163

6.21 ven-Krevlin diagram of various biocrudes obtained in presence of metal loaded Al/SBA-15 (SAR 40) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 166

6.22 TAN and HHV analysis of various biocrudes showing the effect of different noble metals (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10) 167

6.23 FT-IR of various biocrudes showing the effect of different noble metals loaded on Al/SBA-15 (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 168

6.24 Silica adsorption chromatography analysis of biocrudes obtained from insitu upgradation with noble metals loaded on Al/SBA-15 (SAR 40) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 169

6.25 HHV and CHNO analysis of the biocrudes obtained from different loading of Pd on Al/SBA-15 (SAR 40) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 171

6.26 Effect of Catalyst/Biomass ratio (C/B) on the biocrude yield obtained from 5%Pd/AlSBA-15 (SAR 40) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2) 172

7.1	Six lump network system propsed for hydrothermal conversion of *Pongamia* cake.	176
7.2	Various lump yields obtained from catalytic hydrothermal conversion showing effect of temperature (a) P= 20 kg/cm^2 and T = 350^{o}C and (b) P= 20 kg/cm^2 and T = 425^{o}C (W/B =2 and C/B =1:7)	177
7.3	Yield of various lumps obtained from catalytic hydrothermal conversion showing effect of pressure (a) T= 400^{o}C and P= 20 kg/cm^2 (b) T= 400^{o}C and P= 25 kg/cm^2 (W/B =2 and C/B =1:7)	179
7.4	1st rank Deplot obtained for variation in temperature (a) 350 ^{o}C and 20 kg/cm^2 (b) 425^{o}C and 20 kg/cm^2 (t= 35 minutes; W/B =2; C/B =1:7)	180
7.5	1st rank Deplot obtained for variation in pressure (a) 20 kg/cm^2 and 400^{o}C(b) 25 kg/cm^2 and 400^{o}C (t= 35 minutes; W/B =2; C/B =1:7)	181
7.6	2nd rank Deplot obtained for variation in temperature (a) 350 ^{o}C and 20 kg/cm^2 (b) 425^{o}C and 20 kg/cm^2 (t= 35 minutes; W/B =2; C/B =1:7)	181
7.7	2nd rank Deplot obtained for variation in pressure (a) 20 kg/cm^2 and 425^{o}C (b) 25 kg/cm^2 and 425^{o}C (t= 35 minutes; W/B =2; C/B =1:7)	182
7.8	Three lump model for decomposition of biomass to various products.	183
7.9	Four lump model for decomposition of biomass to various products.	183
7.10	Five lump model for decomposition of biomass to various products.	184
7.11	Six lump model for decomposition of biomass to various products.	185
7.12	Estimation of acivation energy from the reaction kinetics for catalytic hydrothermal production of biocrude (P= 25 kg/cm^2 ; t= 35 minutes; W/B =2; C/B =1:7)	189
7.13	Predicted and experimentally obtained yield of various lumps at (a) T= 400^{o}C and P= 20 kg/cm^2 (b) T= 400^{o}C and P= 30 kg/cm^2	191

	(t= 35 minutes; W/B =2; C/B=1:7)	
7.14	Parity plot of all six lump yields obtained at T= 350^oC and P= 20 kg/cm^2. (t= 35 minutes; W/B =2; C/B =1:7)	191
7.15	Parity plot for middel distillate range hydrocarbons (Boiling point 195-324^oC) yield obtained between 350 ^oC-425^oC and 20 kg/cm^2-30 kg/cm^2 (t= 35 minutes; W/B =2; C/B =1:7)	192
7.16	Comparison of biocrude yields from hydrothermal conversion of microalgae (reported) and *Pongamia* seed cake (current work) (P= 25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:7)	193

LIST OF TABLES

Table No.	Title	Page. No.
1.1	Worldwide trend of renewable energy usage between 2004-2013.	3
1.2	Worldwide operating plants for pyrolysis oil biomass to liquid fuel production.	5
2.1	Potential of non-edible oil crop in India.	13
2.2	Cellulose, hemicellulose and lignin composition of waste biomass	17
2.3	Cellulose, hemicellulose and lignin compositions of agro/industry waste biomass.	19
2.4	Proximate and ultimate analysis of various waste biomass used for biofuel production.	21
2.5	Classification of pyrolysis process with typical liquid yield and process parameter range.	24
2.6	Product yields and calorific value of various biocrudes obtained from pyrolysis of waste biomass.	28
2.7	^{1}H NMR analysis of different biomass biocrude obtained from pyrolytic conversion.	30
2.8	FT-IR peaks assigned for different functional group present in biocrude obtained from pyrolytic conversion.	31
2.9	Product analysed from GC/MS of biocrude obtained from pyrolytic conversion of lignin, cellulose and hemicellulose.	32
2.10	Literature review on hydrothermal conversion of different waste biomass.	34
2.11	Quantitative composition of various oxygenated compounds in biocrude.	40
2.12	Property variations for biocrude obtained from hydrothermal conversion, pyrolysis of different biomass and heavy petroleum fraction.	41
2.13	Literature review on effect of Alkali/alkaline earth metals in various forms for biomass conversion to liquid biofuel.	45
2.14	Literature review on effect of organic solvent in various forms for biomass conversion to liquid biofuel.	49
2.15	Physico-chemical characteristics of mesoporous silica.	55

2.16	Literature review on conversion of biomass on microporous/ mesoporous catalysts.	58
2.17	Deoxygenation of biocrude on various supports loaded with noble metals as promoter.	62
2.18	Literature review on various lump models proposed for cracking of heavy hydrocarbon and coal for estimation of kinetic parameters	65
3.1	Experimental conditions used for the preliminary studies on thermochemical processes.	75
4.1	Ultimate, proximate and HHV analysis of seed cakes.	88
4.2	Ultimate analysis of biocrudes obtained from thermochemical conversion of seed cakes (biomass wt =20 g for pyrolysis process); and 50 g for hydrothermal conversion)	97
4.3	Biocrude characterization obtained from hydrothermal conversion (T=400^{o}C P=30 kg/cm^2; t = 40 minutes; W/B=3)	99
4.4	GC/MS analysis of *Jatropha, Pongamia* and Tung biocrude (T=400^{o}C P=30 kg/cm^2; t = 40 minutes; W/B=3)	105
4.5	Ultimate and HHV analysis of *Jatropha, Pongamia* and Tung biochar obtained from hydrothermal conversion. (T=400^{o}C; P=30 kg/cm^2; t= 40 minutes; W/B=3)	109
4.6	GC analysis of gaseous products obtained from hydrothermal conversion. (T=400^{o}C; P=30 kg/cm^2; t=40 minutes; W/B= 3)	114
5.1	Plackett–Burman experimental design matrix for maximization of biocrude yield.	116
5.2	Value of process parameters for different α levels and their actual values.	117
5.3	Design matrix and experimental response for the hydrothermal conversion of Pongamia cake to biocrude.	118
5.4	Regression analysis from CCD technique for biocrude yield and C_6-C_{24} hydrocarbons fraction.	120

5.5 Regression coefficients obtained from the statistical model obtained for quadratic model of biocrude yield and C_6-C_{24} hydrocarbon fraction. 121

6.1 GC/MS analysis (% area) of biocrudes obtained from acetone, ethanol and tetraline (with 50% solvent) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; (W+S)/B =2) 138
6.2 CO_2 fraction in gas products obtained from GC analysis (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2) 141
6.3 Silica gel adsorption chromatography of biocrude obtained in the presence of alkali/alkaline earth metals (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10) 143
6.4 Textural properties of mesoporous catalysts (aluminated and non-aluminated). 147
6.5 Product yield obtained over pure mesoporous catalysts during biocrude upgradation (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B=1:10) 151
6.6 GC analysis of gas phase obtained from insitu hydrothermal catalytic conversion (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 152
6.7 GC analysis of TGF fraction (hydrocarbons below B.P. 391oC) obtained from insitu hydrothermal catalytic conversion of Pongamia seed cake. (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 153
6.8 ^{1}H NMR of upgraded biocrude obtained over aluminated mesoporous catalysts (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 154
6.9 FT-IR analysis of various subfractions of biocrude obtained from catalytic conversion in presence of mesoporous catalysts (SAR 30) (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 156
6.10 Ultimate and HHV analysis of catalytically upgraded biocrudes (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 165
6.11 GC/MC analysis of biocrudes obtained over metal loaded Al/SBA-15 (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 170
6.12 Silica adsorption chromatography of various fractions obtained from vacuum distillation of upgraded biocrudes. (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:10) 172

7.1	Different lump considered for estimation of kinetic parameters on the basis of boiling point range.	171
7.2	Experimentally calculated rate constant of different lumps (T=400^{o}C; P=25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:7)	183
7.3	Activation energy obtained for hydrothermal conversion at different pressure (P= 25 kg/cm^2; t= 35 minutes; W/B =2; C/B =1:7)	185

NOMENCLATURE

ANOVA	Analysis of Variance
ASTM	American Standard Test Method
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner Halenda
CCD	Center Composite Design
CF	Calibration Factor
CHNO	Carbon-Hydrogen-Nitrogen-Oxygen
DOE	Design of Experiment
DP	Dipole Moment Unit
EDX	Energy Dispersive X-Ray
FDU	Fudan University
FID	Flame Ionization Detector
FSM	Folded Sheet Mesoporous Materials
FTIR	Fourier Transform Infrared
GC/MS	Gas Chromatography and Mass Spectroscopy
HHV	High Heating Value, MJ/Kg
HMA	Hexagonal Mesoporous Aluminophosphate
HMS	Hexagonal Mesoporous Silica
HY	Linde Type Y Zeolite
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
KIT	Korean Institute of Technology

MCM	Mobile Composition Of Matter
MFI	Mordenite Framework Inverted
MSU	Michigan State University
NMR	Nuclear Magnetic Resonance
PAH	Polyaromatic Hydrocarbon
RSM	Response Surface Method
SBA	Santa Barbara Amorphous
SAC	Silica Adsorption Chromatography
SAR	Silica To Alumina Ratio
SEM	Scanning Electron Microscope
TAN	Total Acid Number
TAPPI	Technical Association of The Pulp and Paper Industry
TCD	Thermal Conductivity Detector
TEOS	Tetraethyl Ortho Silicate
TGA	Thermogravemetric Analysis
TGF	Transportation Grade Fuel
TMB	Trimethyl Benzene
TMS	Tetramethylsilane
TOC	Total Organic Content
TPR	Temperature Programmed Reduction
XRD	X-ray Difraction
ZSM	Zeolite Socony Mobil

a	mean aggregate surface area per hydrophilic head group
A_i	Independent variable used for optimization study

A_M	area of an atom, cm^2
B	Biomass weight. g
C	Catalyst weight, g
d	separation of lattice planes or metal particle size, mm
D	Unit of dipole moment
D_M	metal dispersion
E_a	Activation Energy, kj/mol
E_{Ai}	Individual effect used for Placket Burman Design
F127	Puronic triblock copolymer
g	Packing factor
H^+	Anionic Silicate species
$I^{-,o,+}$	Anionic, neutral or cationic Silicate species
k_{ij}	Rate constant, min^{-1}
k	number of parameters for process parameter optimization
L	Lump
l	critical hydrophobic chain length
N	Number of Run
P	Operating Pressure, kg/cm^2
P123	Pluronic triblock copolymer
S	Weight of Solvent, g
$S^{+ \text{ or } o}$	Cationic surfactant
t	Run time, minute
T	Temperature, ^oC
V	effective volume of the hydrophobic chain
V_M	bulk atomic volume of the metals, cm^3

W	Weight of water , g
X	Conversion
y	Wt fractions of individual lump
Y	Response or yield
λ	wavelength of incident radiation
θ	incident Bragg angle
α	Process parameter level used for optimization study
κ	regression coefficients