IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

Catalytic Deoxygenation Pyrolysis of Sacha Inchi Shell Over SBA-15 Catalyst: An Analytical PY-GC/MS

Catalytic Deoxygenation Pyrolysis of Sacha Inchi Shell Over SBA-15 Catalyst: An Analytical PY-GC/MS

C Soongprasit[1], D Aht-Ong[1, 2], V Sricharoenchaikul[3] and D Atong[4,*]

[1]Department of Material Science, Faculty of Science, Chulalongkorn University
[2]Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University
[3]Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University
[4]National Metal and Material Technology Center, Thailand Science Park

[*]Email: duangdua@mtec.or.th (Tel.:+662-218-6689)

Abstract. Upgrading of pyrolysis vapors from fast pyrolysis of Sacha inchi shell biomass (SiS) over SBA-15 catalyst (5.81 nm pore diameter) were investigated. SiS had carbon of 41.08% with combustible compounds of 82.25%. Fast pyrolysis of SiS at 400-600 ℃ using SBA-15 as catalyst were performed by Py-GC/MS. The effects of SiS particle size, pyrolysis temperature, and biomass to catalyst ratio (B/C 1:1 and 1:5) strongly affected chemical composition of pyrolysis vapors. Without catalyst, oxygenated compounds were found as major contributor of pyrolysis vapors (60.37-80.11%). Higher pyrolysis temperature and greater amount of catalyst led to increasing of hydrocarbons (aliphatic and aromatic) while nitrogenated compounds, oxygenated compounds and phenol decreased. Significantly improvement on hydrocarbon compounds was observed from 5.46% (thermal condition) to 20.09% and 47.75% when catalysts were added to 1:1 and 1:5 at 500 ℃, respectively. The drawback was that N-compounds increased when amount of catalyst increased. Aromatic HC content was significantly improved when pyrolysis temperature increased from 500 ℃ to 600 ℃, while aliphatic HC reached the maximum at 500 ℃.

1. Introduction

Sacha Inchi (Plukenetia volubills) is a tropical plant in South America and South East Asia, especially Thailand. Its fruit is of green star shaped consists of 3-5 cm diameter capsules with 4-7 green and ripen blackish lobes. Inside the lobes are the seed and oval. Sacha Inchi are new economic plant in Thailand due to their high omega (3, 6, 9), protein, vitamin, and other nutrient that can be used as food supplements. Sacha Inchi seed and oval are extracted to obtain edible bio-oil while its shell is neglected. Based on information from local manufacturer, most of the shell is converted into solid char to be used as fuel for the boiler. Thus, Sacha Inchi shell can potentially be utilized as alternative carbon feedstock for bio-fuel production from fast pyrolysis.

Pyrolysis process is one of promising thermochemical process to convert biomass to liquid fuel. This process is particularly viable environmental friendly approach from its high efficiency and possible closed carbon cycle [1]. Typical biomass to liquid fuel conversion processes begin with pyrolysis, followed by catalytic upgrading of the resulting liquids. In general, bio-oil obtains from conventional pyrolysis contain high carboxylic group and N-compound that results in low pH which leads to corrosion problem when applied as engine fuel. Using catalyst is a practical way to upgrade the quality of bio-oil in which cracking reaction (dehydration, decarboxylation, and decarbonylation) [2] of heavy molecules, oxygenated compound, and N-compound into lighter molecules may be achieved [3]. Catalytic pyrolysis produces superior quality of bio-oil at atmospheric pressure without the need of additional hydrogen as opposed to hydrodeoxygenation process, which makes this process more viable [4].

In this work, catalytic fast pyrolysis of Sacha Inchi shell is performed using Pyrolyzer-Gas Chromatography/Mass Spectrometry (Py-GC/MS) over SBA-15 zeolite catalyst at 400-600 ℃. The aim is to reduce the oxygenated compound, produce hydrocarbons to improve resultant bio-oil. Effect of catalysts loading,pyrolysis temperature, biomass particle size on chemical species of pyrolysis products were discussed.

2. Materials and Methods

2.1. Biomass and catalysts characterization

Sacha Inchi shell (SiS) was collected from oil extraction plant in Kamphaeng Phet province, Thailand. The samples are sun-dried, crushed and sieved into 125 μm, 125-425 μm, and 425-850 μm. Ultimate and proximate analysis were performed by elemental analyzer (LECO; TrueSpec CHN/CHNS) and Thermogravimetric analyzer (METTLER TOLEDO; TGA/STA 851 ᵉ; TGA). Particle size distribution of biomass was determined by particle size analyzer (Malvern; Mastersizer2000). Thermal decomposition behaviour of SiS under nitrogen (N_2) atmosphere was investigated by TGA techniques at 50-900 ℃ with heating rate of 10 ℃/min under N_2. Heating value was determined by Bomb calorimeter (LECO; AC350). Zeolite Santa Babara Amorphous (SBA-15, Sigma-Aldrich) was used as catalysts.Pore size diameter, surface area, and pore volume of SBA-15 were quantified by surface area analyser (Malvern; Autosorb 1-MP). Morphology was observed by Scanning Electron Microscope (Hitachi; FE-SEM SU5000).

2.2. Fast pyrolysis of Sacha Inchi Shell by Py-GC/MS

Catalytic fast pyrolysis of SiS were studied by Pyrolyzer (Frontier; Py-2020iD) with an auto-shot sampler (Frontier; AS-1020E) interfaced to a GC (Shimadzu; GC 2010) with MS (Shimadzu; QP 2010 Plus) at 400-600 ℃. . In each test, SiS sample was restricted to 0.4 mg while the catalyst quantities were varied to achieve biomass to catalysts weight ratio (B/C) of 1:1 and 1:5and placed in the stainless steel crucible covered with glass wool layer. The details of the experimental set up can be found in our previous study elsewhere [5]. Chemical compositions of pyrolysis products were determined by mass spectrometry and identified by comparing with NIST mass spectra database.

3. Results

3.1. Sacha Inchi shell characteristics

Ultimate and proximate analysis of as-received Sacha Inchi shell (SiS) was shown in Table 1 and Table 2. SiS is suitable for bio-oil feedstock as it contained high combustible compound (volatile matter and fixed carbon) of 82.25-86.21% and had approximately 41% carbon content. Heating value (18.55 MJ/kg) was in the same range of other biomass. Moisture, volatile organic compounds (VOCs), and fixed carbon were not greatly different among each size. SiS with particle size of <125 μm size has higher ash content (10.80 wt%) and lower VOCs. Combustible compound (volatile and fixed carbon) is important parameter to determine the potential of biomass feedstock to be used as fuel or carbon resources. All SiS samples contained combustible compound higher than 82.25% which was suitable as feedstock for HC production. Note that SiS with size of <125 μm exhibited more uniform particle size distribution than larger sizes which may contain agglomeration of particulate and fibrous parts.

Thermal decomposition (TGA/DTG) of Sacha Inchi shell of various sizes was illustrated in Figure 1. Decomposition characteristic of biomass shell exhibited four degradation steps. Here, first degradation is evaporation of intrinsic moisture which clearly shown at temperature range of 50-150 ℃. The second degradation responds to decomposition of hemi-cellulose between 200-270 ℃. Major decomposition of cellulose occurred at 270-450 ℃. Lignin decomposes at broader temperature range of 200-900 ℃. Thus, it is not straightforward to find certain point of degradation of lignin. However, minor decomposition at 700-800 ℃ may result from fixed carbon in lignin structure. Based on DTG data, SiS with particle size of <125 μm showed lower decomposition rate than those of larger sizes due to higher amount of ash (10.80%).

Table 1. Ultimate analysis of Sacha Inchi shell.

Biomass	%Weight					Heating value (MJ/Kg)
	C	H	N	S	O	
Sacha Inchi shell	41.08	5.40	1.62	0.33	51.57*	18.55
Jatropha seed shell [6]	50.52	6.15	2.32	-	39.41	20.80
Cassava peel [7]	53.70	7.10	1.20	0.10	37.90	17.90
Palm kernel shell [8]	44.56	5.22	0.40	0.05	49.77	15.60

*O: oxygen and ash

Table 2. Proximate analysis of sieved Sacha Inchi shell.

Size (μm)	%Weight			
	Moisture	VOCs	Fixed C	Ash
125	6.94	68.11	14.14	10.80
125-425	5.63	71.63	14.58	8.16
425-850	6.19	71.58	14.18	8.06

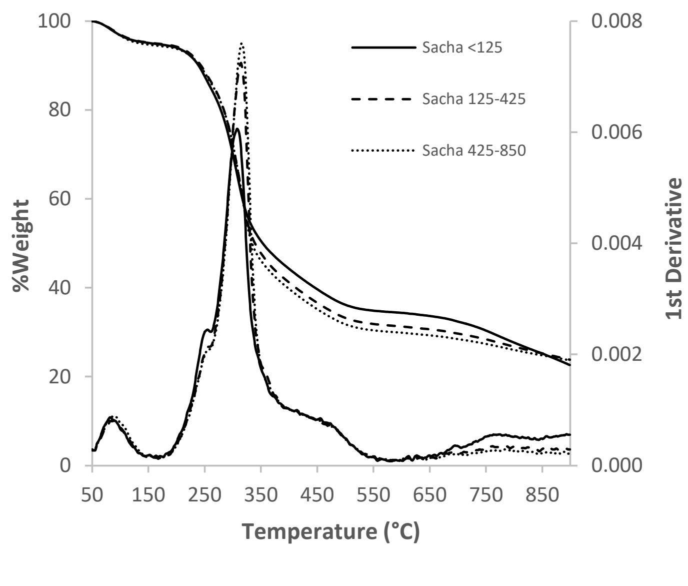

Figure 1. Thermal decomposition profile of SiS.

3.2. SBA-15 catalysts

Unique characteristics of zeolite SBA-15 catalysts are their pore structure that act as acid active site during pyrolysis process. SEM image showed a connection of rod shape particles with length of about 1-2 μm (Figure 2). Surface area, pore volume, and pore size of SBA-15 were 623.5 m^2/g, 1.105 cm^3/g, and 5.810 nm, respectively. Mochizuki and co-workers [9] suggested that small pore size catalysts displayed inferior activity and selectivity on bio-oil production such as decreased aromatic HC yield, and rapid deactivation. From the result, SBA-15 exhibited mesoporous structure (2-50 nm) and should be suitable for improving the quality of bio-oil.

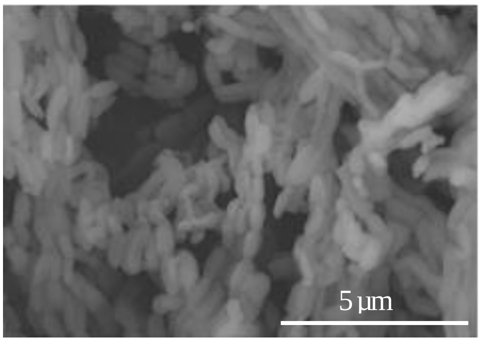

Figure 2. SEM image of SBA-15 catalyst.

3.3.Fast pyrolysis of Sacha Inchi Shell by Py-GC-MS

Pyrolyzed vapors were categorized to various major species, including N-compound, aromatic hydrocarbon, aliphatic HC, oxygenated compound, and phenol. Chromatogram of SiS pyrolysis vapors at 400-600 ℃ were illustrated in Figure 3. At 400 ℃ , highest peak at retention time (RT) of 2.194, 11.918, and 39.483 mins are ketone, phenol and N-compound, respectivelyPeak intensity of these compounds decreased as temperature increased. Oxygenated compounds including ketone, carboxylic acid, ester, ether, aldehyde, and furan are main species produced from pyrolysis under thermal condition (60.37-80.11 Sacha Inchi shell with particle size of 125 µm and 125-425 µm had higher oxygenated compounds than that of 425-850 µm size. Ketone and ester compounds are 40.67% and 11.15%.In general, ketone and ester are derived from hemi-cellulose, and cellulose structures which were degraded to sugar, their repeating unit, and subsequently thermal cracked to ester and ketone, respectively [9]. Note that phenol which generally generated from decomposition of lignin by thermal cracking was found in every conditions. Moreover, SiS with larger particle size, 425-850 µm, showed highest N-compounds.

Higher pyrolysis temperature leads to increasing of aromatic HC and aliphatic HC and results in decreasing of N-compound, O-compound, and phenol. Aromatic and aliphatic HC compounds are decomposed from decarboxylation, decarbonylaion, and dealkylation of oxygenated species. Moreover, dealkylation of phenol compound could results in aromatic HC and aliphatic HC as well. The result indicate that temperature is the one factor, but not dominate, for cracking lignin Sacha Inchi shell.

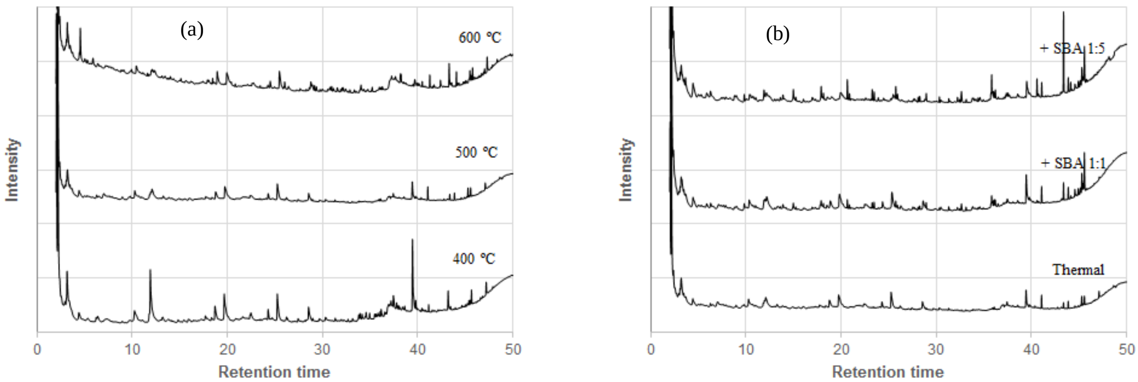

Figure 3. Chromatogram of pyrolysis vapours obtained from fast pyrolysis of SiS 125-425 µm at different (a) temperatures (b) amount of catalyst.

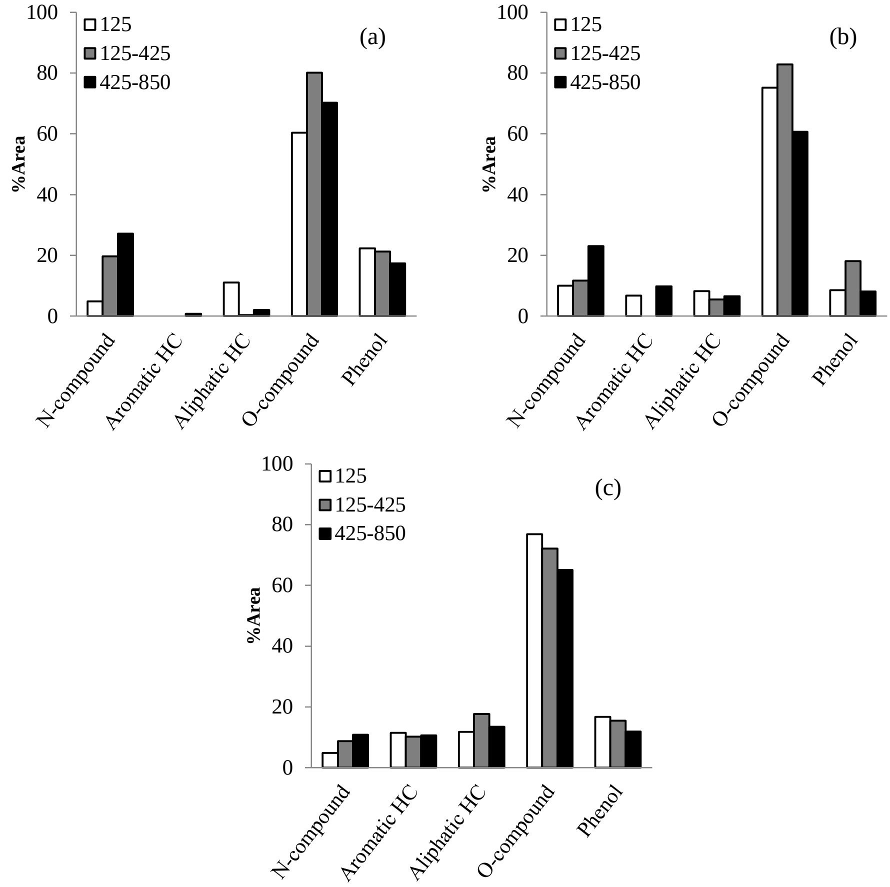

Figure 4. Pyrolysis vapors categorized by chemical species (a) 400 ℃, (b) 500 ℃, and (c) 600 ℃.

The aim of using SBA-15 as catalyst in pyrolysis process is to reduce oxygenated compounds and increase hydrocarbons via selective cracking gas species decomposed from lignocellulosic components. From Figure 3 and Figure 4, pyrolysis product of SiS under thermal and catalytic conditions are clearly different. Generally, phenol compounds generated from lignin have aromatic ring in structure which usually reported to have good thermal stability (more than 1000 ℃). With catalyst, phenol was disappeared at B/C of 1:5. In the other word, SBA-15 can improve cracking of thermally stable species such as lignin derived compounds. The oxygenated compound are main products under thermal condition (80.11%) and drastically reduced to 72.72% and 58.42% when SBA-15 loadings were 1:1 and 1:5, respectively. This reduction of oxygenated compound is found at 500 and 600 ℃. Reduction of O-compound under catalytic pyrolysis is strongly related to the enhancement of aromatic and aliphatic HC produced from decarbonylation, decarboxylation, and deacetylation of oxygenated compound promoted by SBA- 15.

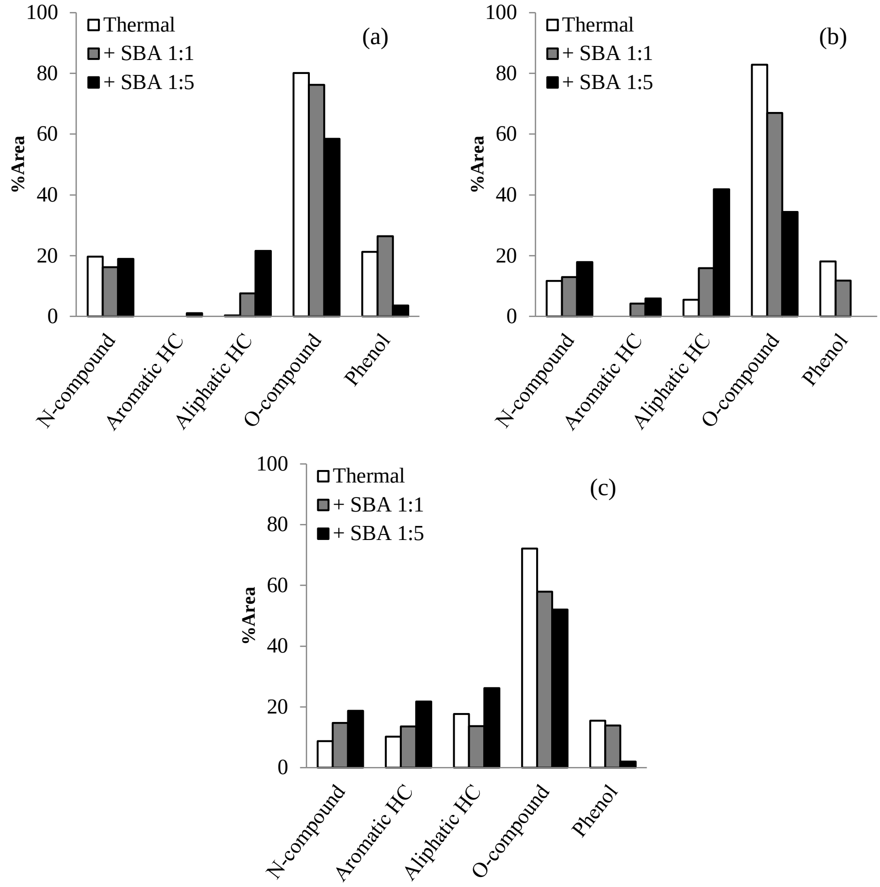

Figure 5. Catalytic fast pyrolysis vapors of Sacha inchi shell 125-425 μm categorized by chemical species (a) 400 ℃, (b) 500 ℃, and (c) 600 ℃.

Pyrolysis temperature also had strong effect on chemical composition of catalysed vapors as shown in Figure 5. Catalytic pyrolysis at 400 ℃ showed low HC (aromatic and aliphatic) yields of 7.56% and 22.68% at B/C1:1 and 1:5 ratio. When catalytic pyrolysis temperature increased, aromatic HC content was considerably improved while aliphatic HC increased and reached the maximum at 500 ℃.Higher catalysts loading clearly showed improvement on HC production. For example, HC yield increase from 5.46% for thermal condition to 20.09% and 47.75% when catalysts was added to 1:1 and 1:5 at 500 ℃, respectively. This results could be explained by active site on SBA-15 is sufficiently high for increasing activity of reactive gas species, especially O-compound and N-compound to react with each other active species leading to formation of deoxygenated compound and results in higher HC yield. Nevertheless, N-compound also significantly increase with catalysts ratio changed from 1:1 to 1:5. This may be a drawback of high catalyst loading in which generation of N-compound may occurred as side reactions. Moreover, reaction to eliminate C-N is more difficult than those of C-C and C-O due to the fact that electrophilic site could not easily be substituted because the electron density of carbon atoms decreases form the electronic effect of nitrogen compound [10].

4. Conclusions

Catalytic fast pyrolysis of SiS wastes using Py-GC/MS were performed to investigate effects of biomass particle size, pyrolysis temperature, and catalyst content on pyrolysis products. The difference in SiS sizes affected pyrolysis products. Significant effect of temperature and catalyst content were also evident. Oxygenated compounds were found as major contributor of pyrolysis vapors at 60.37-80.11% while SiS with particle size of 125 and 125-425 μm sizes had higher oxygenated compound contents than that of 425-850 μm size. Higher pyrolysis temperature led to increasing aromatic and aliphatic HCs and resulted in decreasing of N-compound, O-compound, and phenol. Higher catalyst loadings clearly improved HC production though with higher undesirable N-compound generation. Aromatic HC content was significantly improved when pyrolysis temperature increased from 500 ℃ to 600 ℃, while aliphatic HC reached the maximum at 500 ℃.

Acknowledgement
Authors are grateful to the financial support from the Thailand Graduate Institute of Science and Technology (TGIST, TG-33-09-59-011D), National Metal and Materials Technology Center (MTEC), and Graduate School, Chulalongkorn University.

References
[1] R.P.Anex, A. Aden, F.K. Azi, J. Forman, R.M. Swanson, M.M. Wright, J.A. Satrio, R.C. Brown,D.E.Daugaard, A. Platon, G. Kothandaraman, D.D. Hsu, A. Dutta. Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. Fuel **89** (2010) S29-S35.
[2] S. Thangalazhy-Gopakumar, S. Adhikari, S.A. Chattanathan, R.B. Gupta. Catalytic pyrolysis of green algae for hydrocarbon production using H+ZSM-5 catalyst. Bioresour. Technol. 118 (2012) 150–157.
[3] A. Pattiya, J.O. Tilioye, A.V. Bridewater. Fast pyrolysis of cassava rhizome in the presence of catalyst. J. Anal. Appl. Pyrolysis 81(2008) 72-79.
[4] P.T. Williams, N. Nugranad. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 25 (2000) 493–513.
[5] K. Soongprasit, V. Sricharoenchaikul, D. Atong. Catalytic fast pyrolysis of Millettia (Pongamia) pinnata waste using zeolite Y, J. Anal. Appl. Pyrol. 124 (2017) 656-703.
[6] S.W. Kim, B.S. Koo, J.W. Ryu, J.S. Lee, C.J. Kim, D.H. Lee, G.R. Kim, S. Choi. Bio-oil from the pyrolysis of palm and Jatropha wastes in a fluidized bed. Fuel Process. Technol. 108 (2013) 118-124.
[7] O.L. Ki, A. Kurniawan, C.X. Lin, Y-H. Ju, S. Ismadji. Bio-oil from cassava peel: A potential renewable energy source. Bioresour. Technol. 145 (2013) 157-161.
[8] S-J. Kim, S-H. Jung, J-S. Kim. Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. Bioresour. Technol. 101 (2010) 9294–9300.
[9] T. Mochizuki, S-Y. Chen, M. Toba, Y. Yoshimura. Pyrolyzer-GC/MS system-based analysis of the effect of zeolite catalysts on the fast pyrolysis of Jatropha husk. Appl. Catal., A: General 456 (2013) 174-181.
[10] X. Chen, T. Li, L. Xin, Y. Yang, H. Shan, C. Yang. Inductive effect of basic nitrogen compounds on coke formation during the catalytic cracking process. Catalysis Communications 74 (2016) 95-98.