CHEMICAL ENGINEERING TRANSACTIONS

VOL. 72, 2019

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216

DOI: 10.3303/CET1972024

In-situ Catalytic Upgrading of Pyrolysis Vapours from Sugarcane Bagasse over Newly-developed Ni-Ce/HZSM-5 Catalyst: Effect of Catalyst to Biomass Mass Ratio

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The main objective of this paper is to investigate the influence of catalyst to biomass ratio (by mass %) on the in-situ catalytic upgrading of oxygenated pyrolysis vapours over the newly-developed Nickel-Cerium/HZSM-5 catalyst via in-situ fixed bed reactor. The pyrolysis temperature was kept at 500 °C for all investigated samples. The HZSM-5 (94 wt%) was used as a support, while nickel (3 wt%) and cerium (3 wt%) was impregnated as promoters via incipient wetness impregnation method. The sugarcane bagasse as feedstock was fixed at 2 g, while the catalyst mass loading was loaded and varied in fixed bed reactor based on the catalyst to biomass mass ratio (C:B) as follows 0.5:1.0 (CB1), 1.0:1.0 (CB2), 1.5:1.0 (CB3), 2.0:1.0 (CB4), 2.5:1.0 (CB5), and 3.0:1.0 (CB6). For comparison, the non-catalytic pyrolysis of biomass was employed and labelled as CB0 (0.0:1.0). The results show that the presences of catalyst significantly affect the pyrolysis oil yield than the non-catalytic sample, in which gradually increased from 48.5 wt% to 60.5 wt% with increasing catalyst mass loading from CB1 (0.5:1.0) to CB6 (3.0:1.0). Consequently, the coke yield is also increased from 10.0 wt% to 12.0 wt% from CB1 (0.5:1.0) to CB6 (3.0:1.0). The increase in Ni-Ce/HZSM-5 catalyst mass loading has an additional effect with respect to C_6 – C_8 hydrocarbon contents in pyrolysis oil. Among the tested catalyst to biomass ratio, the CB2 (1.0:1.0) sample has demonstrated to be potential candidates in the enhancement of C_6-C_8 hydrocarbons in pyrolysis oil with the highest yield of 8.82 %.

1. Introduction

Biomass is a biological material frequently referring to plant-derived materials and the only renewable source of organic carbon, in which can be converted into renewable energy via pyrolysis (Vichaphund et al., 2014). For this reason, biomass has widely gained attention from researchers due to potential as a renewable energy resource, sustainability, environmental concerns, and economic reflection (Balasundram et al., 2017a). Interestingly, Galadima and Muraza (2015) reported that pyrolysis of biomass is an inexpensive process due to operating under free oxygen environment and moderate reaction temperature (350 – 700 °C). In addition, pyrolysis of biomass has beneficial effect on maximizing the pyrolysis oil (bio-fuel) yield in the range of 60 – 75 wt% in a single step conversion than non-condensable gas (20 – 30 wt%) and biochar products (15–25 wt%). However, pyrolysis oil has shortcomings such as high viscosity, thermal instability, high corrosiveness, low heating value, and highly contains oxygenated compounds in pyrolysis oil such as anhydrosugars, furans, acids, ester, ether, ketones, aldehydes, alcohols, and phenols that causes limitation in its applications as liquid fuel

Paper Received: 04 March 2018; Revised: 08 August 2018; Accepted: 14 August 2018

Please cite this article as: Balasundram V., Zaman K.K., Ibrahim N., Kasmani R.M., Isha R., Abd Hamid M.K., Hasbullah H., Mohsin R., Ali R.R., 2019, In-situ catalytic upgrading of pyrolysis vapours from sugarcane bagasse over newly-developed ni-ce/hzsm-5 catalyst: effect of catalyst to biomass mass ratio, Chemical Engineering Transactions, 72, 139-144 DOI:10.3303/CET1972024

(Balasundram et al., 2018). Apart from that, pyrolysis oil also has some favourable properties such as less toxicity, good lubricity, and greater biodegradation than conventional petroleum fuels (Zhang et al., 2013).

Galadima and Muraza (2015) reviewed that the catalytic upgrading pyrolysis is highly preferred method to upgrade the oxygenated molecules in pyrolysis vapours into hydrocarbons, in which can be used as gasoline enhancers in the petrochemical industry and high value-added chemical feedstock. For this reason, the addition of catalyst would be a passport for biomass pyrolysis to extend its applications as renewable energy (Zhang et al., 2013). On the other hand, the Hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) catalyst is widely used in oil and chemical industries due to non-corrosive, easy to handle, stable, relatively selective, recyclable, and inexpensive catalyst. Hence, the properties of HZSM-5 catalyst have motivated most scholars to study HZSM-5 as a catalyst in catalytic pyrolysis upgrading process to upgrade the biomass-derived oxygenated pyrolysis vapours (Zhang et al., 2013). In addition, the HZSM-5 catalyst is rich in acid sites that promote the cracking of C-O and C-C bonds of oxygenated compounds through various reactions such as acid-catalysing, deoxygenation, dehydrogenation, dealkylation, and oligomerization (Botas et al., 2014). Consequently, the high acidity of HZSM-5 catalyst could promote the formation of coke that deactivates the catalyst and reduce the selectivity of hydrocarbons in pyrolysis oil. Therefore, the applicability of metal on HZSM-5 was extensively studied by many researchers to further increase the selectivity of hydrocarbons in pyrolysis oil and reduces the rate of coke formation.

Botas et al. (2014) pointed out that among the metals, nickel (Ni) is the most commonly impregnated on HZSM-5 as bi-functional catalyst for catalytic upgrading pyrolysis process due to higher reactivity, low cost, and high availability. Moreover, nickel particles strongly promote the dehydrogenation reaction that favours the formation of hydrocarbons during catalytic upgrading of biomass-derived oxygenated pyrolysis vapours. Similarly, Vichaphund et al. (2014) claimed that the impregnation of nickel on HZSM-5 had significantly improved the selectivity of hydrocarbons in pyrolysis oil than HZSM-5 catalyst. In contrast, Balasundram et al. (2017b) reported that the greater cracking ability of nickel become overwhelming due to the enhanced polymerization (secondary cracking) of oxygenated molecules into heavy compounds, as result settled on the surface of catalyst as coke and blocked the active acid sites of catalyst. Hence, the formation of coke must be solved in order to extend the catalyst's lifetime for more conversion of oxygenated compounds into hydrocarbons. Interestingly, Isha and Williams (2012) reported that cerium (rare earth metal) has beneficial characteristics of oxygen storage capacity that suppress the formation of coke during pyrolysis. Other than that, rare earth metal could inhibit the dealumination process of HZSM-5 during calcination, thus a higher concentration of acid sites is sustained that improves the cracking activity and hydrothermal stability (Balasundram et al., 2018).

Overall, based on cited previous works, nickel (Ni) has a promising effect on the catalytic upgrading of oxygenated pyrolysis vapours into hydrocarbons, while cerium (Ce) has great influence on suppressing the formation of coke. In addition, most of the literatures reported on the effect of single metal loaded on HZSM-5 as bi-functional catalyst on the catalytic upgrading of oxygenated pyrolysis vapours into hydrocarbons. Therefore, in this study, nickel and cerium are impregnated on HZSM-5 to form a novel multifunctional catalyst. The concept of developing a multifunctional catalyst is to acid-catalyzed, deoxygenate, and simultaneously suppress the formation of coke during the catalytic upgrading of oxygenated pyrolysis vapours into hydrocarbons in pyrolysis oil. To the best of our knowledge, the comprehensive study on the effect of catalyst to biomass mass ratio over Ni-Ce/HZSM-5 multifunctional catalyst on the in-situ catalytic upgrading of the oxygenated pyrolysis vapours into hydrocarbons in pyrolysis oil via fixed bed reactor is lacking in the literature. Thus, in this work, the influence of catalyst to biomass mass ratio (0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, 2.5:1.0, and 3.0:1.0) over the Ni-Ce/HZSM-5 multifunctional catalyst on pyrolysis products yield distribution and relative contents of hydrocarbons specifically C_6 – C_8 hydrocarbons in pyrolysis oil was investigated.

2. Materials and methods

2.1 Biomass feedstock preparation

Sugarcane bagasse (SB) sample was selected as biomass pyrolysis feedstock. The SB samples were collected from the local market in Johor, Malaysia. First, the samples were grinded and sieved to obtain a particle size of less than 0.5 mm. Next, the samples were dried at 105 ± 2 °C in a microwave oven for about 24 h until the weight remained constant. The samples were then kept in a desiccator to minimize the absorption of moisture from surrounding humidity. Prior to each experimental run, the sample was dried again in a microwave oven for about 12 h at 105 ± 2 °C. The characterization of sugarcane bagasse such as proximate analysis, ultimate analysis, and calorific value is reported in our previous work (Balasundram et al., 2018).

2.2 Catalyst preparation

The solid powder ZSM-5 (SiO_2/Al_2O_3 mole ratio = 23:1) in ammonium form (NH_4^+) was purchased from Alfa Aesar. The crystalline powders of Nickel (II) Nitrate Hexahydrate, Ni $(NO_3)_2.6H_2O$ (Purity = 99.0 %) and Cerium

(III) Nitrate Hexahydrate, Ce $(NO_3)_3.6H_2O$ (Purity = 99.5 %) were purchased from ACROS Organics. First, the ZSM-5 (NH_4^+) in ammonium form was converted into the protonic form of zeolite (HZSM-5) by calcination at a temperature of 600 °C for 4 hours in the static air (ramp rate = 5 °C/min). The calcination was done in laboratory muffle furnace. Next, the impregnation of nickel (Ni) from Nickel (II) Nitrate Hexahydrate and cerium (Ce) from Cerium (III) Nitrate Hexahydrate on HZSM-5 was achieved via incipient wetness impregnation (IWI) method. The weight percent (wt%) of HZSM-5, nickel (Ni), and cerium (Ce) was fixed at 94, 3, and 3 wt%. After that, all the mass of three chemicals were mixed in a beaker with 80 mL of deionized water and stirred using magnetic stirrer hot plate at a fixed temperature of 80 °C for 4 h. Next, the formed paste was dried in a microwave oven at a temperature of 105 ± 2 °C at about 12 h. Then, the formed solid paste was calcined in a muffle furnace at 600 °C for 4 h (ramp rate = 5 °C/min). Finally, a mortar and pestle were used to crush the solid catalyst. The catalyst was activated at 600 °C with nitrogen flow for 1 h before testing.

2.3 Experimental setup

The newly developed lab-scale fixed bed stainless steel pyrolysis reactor was used to conduct the batch experiments of in-situ catalytic pyrolysis of SB as shown in Figure 1. The experiments were performed in batch runs with varying catalyst mass loading. In detail, the SB sample was fixed at 2 g, while the catalyst mass loading was calculated based on the catalyst to biomass mass ratios as follows 0.5:1.0 (CB1), 1.0:1.0 (CB2), 1.5:1.0 (CB3), 2.0:1.0 (CB4), 2.5:1.0 (CB5), and 3.0:1.0 (CB6). Hence, prior to each experiment, the synthesized catalyst was added first into bed material and followed by sugarcane bagasse (SB) sample (note: quartz wool is used to separate catalyst and biomass). For comparison, the non-catalytic pyrolysis of SB was employed at the same operating conditions and labeled as CB0 (0.0:1.0). The pyrolysis reaction temperature was fixed at 500 °C. The bed material was equipped with a stainless-steel net mesh at the end to support the sample for each run. All the outlet and inlet fittings were tightened to prevent any form of leakage during an experimental run. An inert atmosphere was created inside the reactor by purging nitrogen stream flowing downstream at a rate of 50 mL/min. The atmospheric pressure (1 atm) was maintained throughout the experiment. For each run, the experiment was conducted for 1 h. The generated volatile products in the reactor were purged downward by a nitrogen stream and flow into the condenser (filtering flask). The condensation system was set up by immersing filtering flask into a cold water bath at 5 ± 2 °C. The condensed pyrolysis oil was then collected and further analysed for organic compositions in pyrolysis oil. In order to make experimental results objective, each test was repeated at least three times and average data values were utilized.

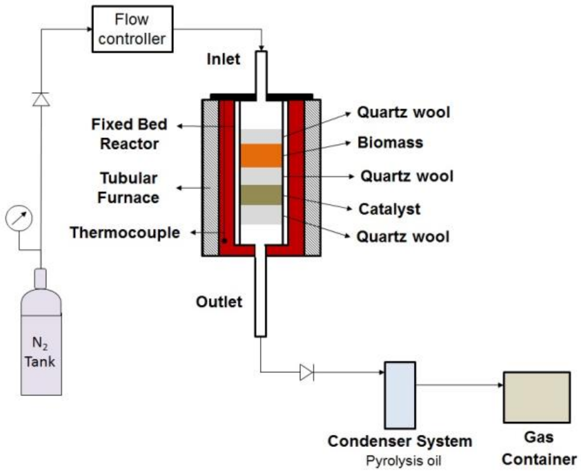

Figure 1: Schematic diagram of pyrolysis experiment set-up

2.4 Characterization of pyrolysis oil

The organic compositions of pyrolysis oil were analysed via gas chromatography-mass spectrometry (GC/MS) (Agilent 6890N series GC with a 5973N Inert MS detector and 7683 Injector). First, CH_3OH solution was used to dilute the pyrolysis oil in a ratio of 1:1 for GC/MS analysis. Then, the GC separation was performed using a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The prepared sample (1 μL) was injected into injection port set at 250 °C in a 1:50 split mode. High purity of helium (He) (99.99 %) was employed as a carrier gas in the column at a constant flow rate of 1.2 mL/min. The column temperature was set at 40 °C for 5 min before it was increased up to 100 °C at 20 °C/min and then to 250 °C at 5 °C/min. The mass spectrometer ion source was operated at 250 °C with 70 eV in electron impact (EI) mode. The mass spectrometer was conducted in scan mode in the range of 30-500 m/z. The chromatographic peaks were discriminated and analysed by means of the National Institute of Standards and Technology (NIST) mass spectral data library. The relative content of each component in the pyrolysis oil was determined by calculating the chromatographic area percentage.

3. Results and discussion

3.1 Effect of catalyst to biomass mass ratio

The influence of catalyst to biomass mass ratio on the in-situ catalytic upgrading of oxygenated pyrolysis vapours from pyrolysis of sugarcane bagasse (SB) was investigated and the results id shown in Figure 2. The pyrolysis products yield is given within the standard deviation of < ± 3 %. The pyrolysis oil yield, non-condensable gas yield, and char yield for CB0 were 50.0, 29.0, and 21.0 wt%. As shown in Figure 2, there is a noticeable effect of catalyst mass loading on the pyrolysis products yield specifically pyrolysis oil yield. For example, the pyrolysis oil yield gradually increased from 48.5 wt% to 60.5 wt. % with increasing catalyst mass loading from CB1 (0.5:1.0) to CB6 (3.0:1.0). This is in line with the gradual decrease of char yield from 22.0 wt% (CB1) to 9.00 wt% (CB6) as shown in Figure 2. Therefore, the thermal cracking of SB into condensable pyrolysis vapours was enhanced to some extent when added more mass of catalyst. This might be due to the influence of high contents of acid sites present at higher catalyst mass loading. Thus, the exposures of thermally evolved volatiles on high content of acid sites were greatly acid-catalyzed and deoxygenated into condensable pyrolysis vapours. This is in line with our previous work (Balasundram et al., 2018). It was also observed that the presence of catalyst had greatly reduced the non-condensable gas yield. In addition, Bi et al. (2011) reported that the cerium particles on HZSM-5 had strongly enhanced the degradation of biomass into pyrolysis oil and inhibit the re-adsorption of volatiles for secondary cracking into gas products on metal sites.

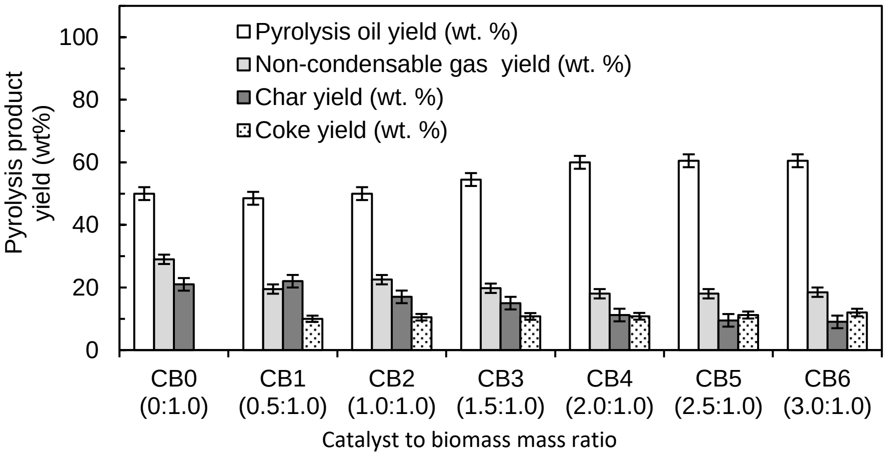

Figure 2: The effect of catalyst to biomass mass ratio

Meanwhile, the pyrolysis oil yield remained constant from CB4 (2.0:1.0) to CB6 (3.0:1.0) as shown in Figure 2. Thus, the catalytic activity of Ni-Ce/HZSM-5 catalyst on biomass has achieved the optimum catalytic cracking from CB4 to CB6. Thus, it can be concluded that the catalyst mass loading at CB5 and CB6 are in an excessive amount to achieve a similar yield of pyrolysis oil that obtained at CB4. On the other hand, Figure 2 illustrates that the non-condensable gas yields were fluctuating in the range of 18.0–22.5 wt% from CB1 to CB6. However, the analysis of the non-condensable gaseous was not performed in this research. The highest non-condensable gas yield (22.5 wt%) was observed at CB2 (2.0:1.0) mass ratio compared to other catalytic samples (refer Figure 2). Interestingly, the CB0 sample (non-catalytic) and CB2 has similar pyrolysis oil yield but has significant differences of 6.5 wt% on the non-condensable gas yield. Similarly, other catalytic samples also had produced lower yield of non-condensable gas than CB0 sample that might be due further polymerization of non-condensable volatiles into coke materials. In addition, the coke yield increased with increasing catalyst mass loading on biomass as shown in Figure 2. Balasundram et al. (2018) claimed that an excess amount of catalyst could block volatiles in its pores thus exposes them at a high temperature in which promotes oligomerization and polymerization into coke materials. Overall, it can be concluded that the increment of catalyst mass loading resulted in higher yield of pyrolysis oil.

3.2 Distribution of hydrocarbons in pyrolysis oil

The effect of catalyst to biomass mass ratio on the distribution of hydrocarbon contents in pyrolysis oil is illustrated in Figure 3. The hydrocarbon content in pyrolysis oil is defined as percentage area (%). The hydrocarbons are grouped based on their total carbon atom numbers (C) such as C_6, C_7, C_8, C_9, and C_{10+} (C_{10} and above). Botas et al. (2014) claimed that the C_6, C_7, and C_8 hydrocarbons are the desirable hydrocarbons to be used as gasoline booster in the petrochemical industry. They also reported that the C_9 and C_{10+} hydrocarbons have a higher viscosity that is more suitable to be used as aviation fuel. In addition, C_{10+} hydrocarbons are also contained polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and its derivatives that act as coke precursors, leading to catalyst deactivation during catalytic upgrading of pyrolysis vapours (Balasundram et al., 2018). Hence, the enhancement of C_6 – C_8 hydrocarbons in pyrolysis oil is the target pursued in this research. The highest content of C_6 to C_{10+} hydrocarbons (13.78 %) in pyrolysis oil was achieved at CB2 mass ratio. In detail, the C_6, C_7, C_8, C_9, and C_{10+} hydrocarbons were at 0.40, 4.11, 4.31, 1.80, and 3.16 % at CB2 mass ratio. Moreover, the CB2 mass ratio has achieved the highest total relative contents of C_6 – C_8 hydrocarbons at 8.82 %.

The reduction of about 65 – 75 % of C_6-C_8 hydrocarbons in pyrolysis oil was observed for other catalyst to biomass mass ratio conditions. In detail, increase in catalyst mass loading from CB1 to CB2 had enhanced the C_6 – C_8 hydrocarbons, however the contents of C_6 – C_8 hydrocarbons in pyrolysis oil decreased when further increase in catalyst mass loading from CB3 to CB6.

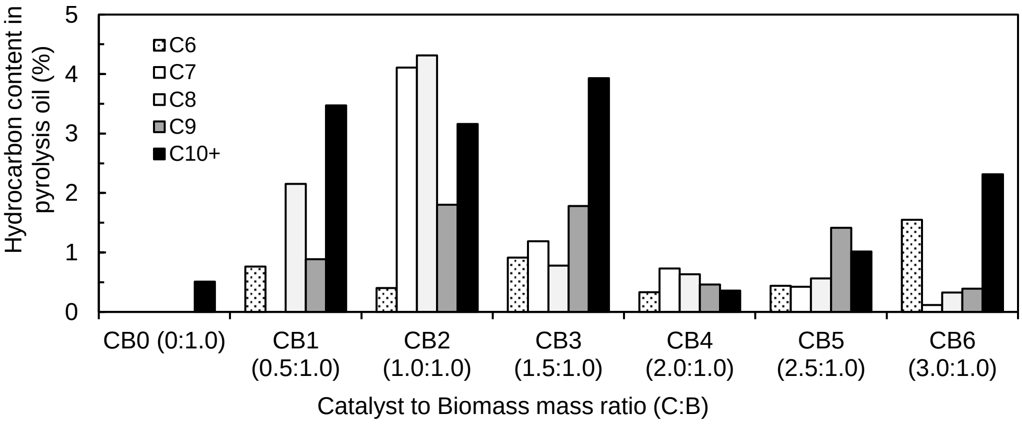

Figure 3: The effect of catalyst to biomass mass ratio on hydrocarbons content (%) in pyrolysis oil

Moreover, it was noticed that the production of the total content of C_7 and C_8 hydrocarbons were highly favourable than C_6 hydrocarbons at all catalyst to biomass mass ratios. This might be due to the additional effect by nickel in Ni-Ce/HZSM-5 catalyst that favours the alkylation of C_6 hydrocarbons into C_7 and C_8 hydrocarbons. This result is in agreement with previous works, which reveal that the presence of nickel promotes the alkylation of small hydrocarbons into large hydrocarbons (Thangalazhy-Gopakumar et al., 2012). The CB6 mass ratio highly generates C_6 hydrocarbon (1.55 %) than C_7 and C_8 hydrocarbons in pyrolysis oil as shown in Figure 3. This might be due to the excessive amount of acid sites of metal (nickel) that might highly favour the cracking of oxygenates into C_6 hydrocarbons and oligomerization or alkylation of C_7 to C_9 hydrocarbons into C_{10+} hydrocarbons. However, it was observed that the C_{10+} hydrocarbons were largely produced in the range of 3.16 – 3.93 % at CB1 to CB3 mass ratios as illustrated in Figure 3.

A similar study by Vichaphund et al. (2014) stated that the presence of nickel as transition metal on HZSM-5 had enhanced the alkylation of short chain hydrocarbons into long chain hydrocarbons. Consequently, these bulky compounds might continuously accumulate on the internal and external surface of catalyst that blocks the diffusion pathway of volatiles, leading to increasing in coke formation. This is in line with the gradual increase in coke yield when increased the catalyst mass loading from CB1 to CB6 (refer Figure 2).

Overall, the increasing performance of catalyst mass loading ratio on upgrading the oxygenated pyrolysis vapours into C_6 – C_8 hydrocarbons over Ni-Ce/HZSM-5 catalyst is ranked in the following order: CB2 (8.82 %) > CB1 (2.92 %) > CB3 (2.88 %) > CB6 (1.99 %) > CB4 (1.70 %) > CB5 (1.43 %). Hence, the increase in catalyst mass loading after CB2 had negatively affects the formation of C_6 – C_8 hydrocarbons, while favours the formation of C_{10+} hydrocarbons and coke.

4. Conclusion

The in-situ catalytic upgrading of oxygenated pyrolysis vapours from sugarcane bagasse has been successfully conducted to investigate the influence of catalyst to biomass ratio (C:B) over Ni-Ce/HZSM-5 multifunctional catalysts on pyrolysis products yield and distribution of organic compounds specifically the contents of C_6 – C_8 hydrocarbons in pyrolysis oil. The presence of catalyst has beneficial effect on producing higher yield of pyrolysis oil with increasing catalyst to biomass ratio from CB1 (0.5:1.0) to CB6 (3.0:1.0) in the range of 48.5 wt% to 60.0 wt%. However, the increase in catalyst mass loading has side effect on increasing the coke yield from 10.0 wt% (CB1) to 12.0 wt% (CB6). Meanwhile, the highest content of C_6 – C_8 hydrocarbons in pyrolysis oil can be achieved at catalyst to biomass mass ratio of 1:1 (CB2) over the Ni-Ce/HZSM-5 catalyst. In conclusion, the results obtained in this work show that by a convenient selection of catalyst to biomass ratio, it is possible to upgrade oxygenated pyrolysis vapours into C_6 – C_8 hydrocarbons.

Acknowledgments

The authors would like to acknowledge the financial supports by Universiti Teknologi Malaysia, Ministry of Higher Education (MOHE) of Malaysia (Q.J130000.2546.20H18 and Q.J130000.2546.14H48) and Universiti Malaysia Pahang (RDU1703242).

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