CATALYTIC UPGRADING OF PYROLYSIS VAPORS FROM JATROPHA WASTES USING ALUMINA, ZIRCONIA AND TITANIA BASED CATALYSTS

P. Kaewpengkrow¹, D. Atong² and V. Sricharoenchaikul^{1,3*}

¹*Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn
University, Bangkok, Thailand*

²*National Metal and Materials Technology Center, Pathumthani, Thailand*

³*Center of Excellence on Hazardous Substance Management (HSM), Thailand*

* *Corresponding author. Tel.: +66-2-218-6689; Fax: +62-2-218-6666, E-mail:
viboon.sr@chula.ac.th*

ABSTRACT. The objective of this study was to catalytically upgrade bio-oil from organic vapors of Jatropha wastes using Py-GC/MS. Catalytic testing included Al₂O₃, ZrO₂, TiO₂ (rutile, T₁) and TiO₂ (anatase, T₂) supporter catalysts modified with transition metals (Pd, Ru or Ni) by impregnation method. In non-catalytic runs, the main vapor products were fatty acids (60.74%). With the presence of Al₂O₃ based catalysts, carboxylic acids were obviously reduced to 0.76-19.61% while hydrocarbons were the main products (42.00-64.06%). Comparing among four supporters, total hydrocarbon yields increased with presence of all catalysts. Higher yields were obtained by T₂>Al₂O₃>CA>NiCA>RuCA catalysts. Al₂O₃ and T₂ supports were the most effective for increased hydrocarbons while decreased oxygenated compounds (15%) which is one of the primary aims of this study. The result indicating that high surface area resulted in better catalytic activity but also adversely promoted N-compounds. Therefore these catalysts can be applied to improve properties of pyrolytic products.

Keywords: *Catalyst, Jatropha wastes, Pyrolysis vapors, Upgrading*

1. Introduction

Biomass derived fuels could be the promising fuel of the future which can be produced within a relatively short cycle and are considered sound for the environment (Mortensena et al., 2011). These renewable sources can become partial alternative to crude oil for production of high quality transportation fuels. They also help on reducing the dependence on petroleum as well as carbon dioxide emissions which responsible for the greenhouse effect (Gracía et al., 2013). In recent years, Jatropha plant has been widely gaining attentions as a potential renewable energy crop in which its extracted oil may be used directly with slow speed diesel engine or upgraded via transesterification to conventional biodiesel (Murata et al., 2012). Oil yields of about 30–40% can be obtained from extraction of Jatropha seed. Generally, this oil has similar properties to that of palm oil (Abdul Khalil et al., 2013). However, unlike other edible oils, Jatropha oil is toxic and not included in general food matrix or food chain. This is of primary importance since utilization of edible plants as energy source would raise both ethical and sustainable questions.

Jatropha wastes from biodiesel production process are needed to be collected and disposed. Fast pyrolysis is a process developed to directly convert biomass feedstocks into liquid products as bio-oil. This oil has several potential applications such as heat and power generation and also as a feedstock for various chemical processes. However, it cannot be directly used as transportation fuels due to some undesired properties such as oxygen-rich composition, low heating value, immiscibility, corrosiveness, etc. Bio-oil, in its present form, may be upgraded to be used as a liquid transportation fuel (Srinivasan et al., 2012). Therefore, if Jatropha residues can be effectively converted to

liquid product, the Jatropha plant would become an economically valuable alternative source of biofuels (Mochizuki et al., 2013b).

There are several methods of upgrading and improving bio-oils quality. Some proposed methods are the catalytic cracking through hydrotreatment, deoxygenation or decarboxylation. The catalytic cracking of bio-oils removes oxygen by simultaneous deoxygenation reactions as follows:

These reactions are similar to petroleum refining with conventional metal catalysts (Co, Mo, and Ni). This is the most probable route to remove the oxygen containing functional groups of bio-oils and hence convert the oxygenated compounds to a lighter hydrocarbon fraction and higher aromatic contents (Gracia et al., 2013). Moreover, the most promising processes for the continuous biomass catalytic conversion to bio-oil requires catalyst regeneration capability. Consequently, upgrading of bio-oil by catalytic reforming of pyrolytic vapors product was to be studied in this work. In early researches, zeolites have been widely studied on upgrading of fast pyrolysis vapors by Py-GC/MS, such as HZSM-5 and Al/SBA-15 (Murata et al., 2012; Srinivasan et al., 2012; Thangalazhy-Gopakumar et al., 2011; Pattiya et al., 2008; Qiang et al., 2009) which are effective to convert the highly oxygenated compounds to aromatic hydrocarbons. Pattiya et al. (2008) tested the catalytic effects on cassava rhizome, the result showed that catalysts produced aromatic hydrocarbons and reduced oxygenated lignin derivatives. Murata et al. (2012) studied fast pyrolysis of Jatropha wastes, the result showed that aromatics are largely formed above 90% of overall GC peak area by using catalysts (H-ZSM-5 and zeolites). Zhang et al. (2013) added mesoporous catalysts

(γ -Al₂O₃) in the microporous catalyst (LOSA-1) for biomass catalytic pyrolysis and found that these catalysts could improve the hydrocarbon selectivity with the maximum aromatic and olefin yield of 25.3%. However zeolites are difficult to synthesized and also inherit high production cost. They are difficult to be industrially utilized for upgrading biomass pyrolysis vapors.

Recently, some transition metal based catalysts such as Ni, Co, Pt, Pd and Ru catalysts are utilized for deoxygenated reactions which were reported by several researches (Bulushev and Ross 2011; Choudhary and Phillips, 2011; Lu et al., 2010; Ying et al., 2012; Zhang et al., 2013). Modification of metal catalysts on ceramic support are generally performed by the impregnation method which inherits low production cost and fine hydrothermal stability as reported by Lu et al. (2010) and Kaewpengkrow et al. (2014) who used the transition metal with ceramic supports. They found that these catalysts enhanced yields of aliphatic and aromatic hydrocarbons to 10-40%. In addition there have been some works using ceria (CeO₂) based catalysts, mostly for promotion of hydrogen production and prevention of coke deposition during the gasification and pyrolysis process (Bulushev and Ross, 2011; Kaewpengkrow et al., 2014). Metals such as Ni, Pd, and Ru have been added to the ceria-based catalyst system to improve the catalytic performance. For this reason, Ce-based modified catalysts as a promoter were synthesized in this study. The superior activity and stability of these catalysts would further enhance the fast pyrolysis sequential process.

A pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) system was used to investigate the effect of metals on four supporters and Jatropha waste to catalyst ratios (J/C) on the evolved pyrolysis vapors. The primary aim of this study is to reduce the oxygen content in subsequent pyrolysis products.

2. Material And Methods

2.1 Biomass Preparation

Jatropha wastes used in the current study was obtained from local plants in Chiangrai province in northern Thailand. These wastes were discarded after extraction of oil from biodiesel production process. Properties of Jatropha wastes including proximate and elemental analyses, higher heating values (HHV) and chemical compositions were determined. Jatropha wastes was first separated from physical impurities and dried at 60°C to reduce moisture prior to any subsequent analyses. The dried sample was crushed with a grinder equipped with 3 mm-mesh. It was then passed through sieves to obtain particle size of less than 125 µm and dried for 24 h at 110°C in the oven. The biomass feedstock main characteristics are shown in Table 1. The proximate analysis was performed following the American Society for Testing and Materials (ASTM) to classify the sample in terms of moisture (ASTM E871, 2006), volatile matter and fixed carbon (ASTM E872, 2006), and ash (ASTM D1102, 2007). The high volatile organic matter (73.80%) indicating that Jatropha waste should be a good candidate for the production of liquid fuel. Bomb calorimeter (Leco model AC-350) was used to determine the higher (gross) heating value of raw material following ASTM D240 (2009).

The ultimate analysis was carried out using Leco TruSpec[®] CHNS (micro) analyzer which reported the composition of Jatropha in weight percentage of carbon, hydrogen, sulfur, nitrogen and oxygen. Similar to typical biomass, carbon (49.03 wt.%) is the main element of this waste. The oxygen content is also considerably high which could yield unfavorable oxygenated pyrolysis liquid products. However, one advantage of this

waste is its low sulfur content which suggests that it is suitable for production of liquid fuel with high energy content and low sulfur by-products. Obviously, the nitrogen element in *Jatropha* is higher than other woody biomass. Nitrogen plays a major role as a precursor for the formation of N-containing compounds in the fuel product which may be corrosive substances, thus not suitable for the engines (Kaewpengkrow et al., 2014). The empirical formula based on the elemental analysis of *Jatropha* waste was $C_7H_{13}O_4N$.

Generally pyrolysis of biomass is significantly dependent on its main components of cellulose, hemicelluloses and lignin. The chemical compositions of these three main components were also identified using TAPPI T203 (1999) and T222 (2006) standard methods. *Jatropha* waste contains large amount of hemicellulose (59.20%) with much lesser cellulose and lignin of 18.00% and 22.80%, respectively, suggesting that this waste can be effectively converted into liquid fuel by pyrolysis process at relatively low temperature.

2.2 Synthesis and Characterization of Catalysts

Catalytic testing included Al_2O_3 , ZrO_2 , TiO_2 (rutile, T_1) and TiO_2 (anatase, T_2) support catalysts. Catalyst preparation was initiated by stirring mixture of cerium (III) nitrate solution and Al_2O_3 support at 300 rpm for 3 h at 80°C and then dried at 110°C for 24 h. The dried $Ce(NO_3)_3/Al_2O_3$ was calcined in air at 700°C for 4 h to obtain 6% CeO_2/Al_2O_3 (CA) as promotor to achieve well dispersion of the transition metal. After that, palladium nitrate (or ruthenium chloride hydrate, nickel nitrate) was then impregnated on CeO_2/Al_2O_3 catalyst by the same method. The catalysts contained 1.0 wt.% metal (Pd, Ru or Ni) on 6% CeO_2/Al_2O_3 catalyst. Finally, the synthesized catalysts

were 1%Pd-6%CeO₂/Al₂O₃, 1%Ru-6%CeO₂/Al₂O₃ and 1%Ni-6%CeO₂/Al₂O₃ which referred to as PdCA, RuCA and NiCA, respectively, making a total of twenty prepared catalysts to be tested in this study. Physical properties of various supports are shown in Table 2. The absorption characteristics of catalysts were obtained by N₂ adsorption measurements using the BET equation for the determination of surface area. Surface area of the Al₂O₃ based catalysts (85.81-90.35 m²/g) were slightly lower than that of the support (103.38 m²/g) while surface area of T₂ based catalysts were obviously reduced from 204.25 to 33.34-45.91 m²/g. Among four catalyst groups, alumina based catalyst has the highest surface area while those of ZrO₂ and T₁ supported catalysts did not change when compared to their respective supports. The morphology of catalysts synthesized with various supports were investigated by SEM analysis, conducted after calcination at 700°C. SEM shows contrast due to the topology and composition of the surface. Particles of Al₂O₃ ZrO₂ and T₁ based catalysts were agglomerated to the size of more than 1 µm while those of T₂ based catalysts were agglomerated to the size of less than 1 µm. This result corresponds well with particle size analysis. Energy dispersive X-ray (EDX) analysis was also used to approximate the amount of several elements. The metal loading contents on alumina (1.07-1.19%), zirconia (1.64-2.01%) rutile (0.61-0.82%) and anatase (0.77-1.32%) were found to be relatively right on target and finely distributed over the surface.

Estimation of the amount of element was carried out using X-ray elemental analysis, X'Pert Pro MPD diffract meter with a Cu Ka radiation operated at 40 kV and 40 mA. It was found that the highest peak matched the monoclinic structure of ZrO₂ according to JCPDS: 37-1484. The highest peak intensity of support corresponded to the tetragonal structure of Al₂O₃, T₁ and T₂ according to JCPDS: 46-1131, 21-1276 and 21-1272

respectively. After impregnating with cerium nitrate solution, the peaks at 2θ corresponded to the CeO_2 cubic phase (JCPDS: 34-0394) were observed. When further doping with various active species, the small peaks of Pd, Ru and Ni doped catalyst were indexed as tetragonal of PdO phase (JCPDS: 34-1101), and RuO_2 phase (JCPDS: 40-1290), and hexagonal of NiO phase (JCPDS: 44-1159), respectively.

2.3 Catalytic fast pyrolysis of Jatropha wastes

Twenty catalyst samples were used to investigate their influence on pyrolysis product distribution and then to predict the change in bio-oil properties. The pyrolysis of Jatropha wastes with size less than $125\text{ }\mu\text{m}$ were performed at 600°C in a Py-GC/MS. These experiments were carried out in a pyroprobe (multifunctional pyrolyzer, PY-2020iD, Frontier Lab) with auto-shot sampler AS-1020E interfaced to a gas chromatograph coupled to a mass selective detector (GCMS- QP2010, Shimadzu) to separate and identify the evolved products. The sample was placed in a sample cup and the catalyst was placed above the Jatropha wastes and then dropped into the heated zone of pyroprobe and hold for 0.50 min. In a typical run, the amount of Jatropha wastes was 0.40 mg and catalysts used were 0.4, 2.0 and 4.0 mg to obtain J/C ratio of 1:1, 1:5 and 1:10 for Al_2O_3 support, respectively, while the J/C ratio of 1:10 was fixed for other supports. The GC separation was carried out by an ultra-alloy capillary column (UA5-30M-0.25F, 30m, 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was used as a carrier gas with a gas flow rate of 1.1 mL/min, and the split injector ratio of 1:50. During the analysis of the pyrolytic products, the oven temperature was started from 50°C (3 min) to 200°C (heating rate of $5^\circ\text{C}/\text{min}$) then to 350°C (heating rate of $5^\circ\text{C}/\text{min}$) and hold for 10 min. The injector and detector temperature was kept at 280°C .

The separated compounds were then analyzed using a mass selective detector operating in electron impact mode (EI) at 70 eV from mass ions (m/z) of 20-800. Identification of spectra was carried out by matching the mass ions of each peak with NIST mass spectral database.

3. Results And Discussion

3.1 Effect of J/C ratio on pyrolytic product

The main focus of this section is on active metal doped on alumina (Al_2O_3) supporter. The pyrolysis of Jatropha residue was carried out at 600°C with J/C ratio of 1:1, 1:5 and 1:10. The pyrolytic products were represented by quantification percentages of relative peak area of each compound with retention time obtained from the chromatogram. Products were grouped into different categories such as aromatics, hydrocarbon compounds, oxygenated compounds (included alcohol, aldehyde, ether, ester, furan, ketone and phenol), N-compounds and sugars (levoglucosan and α -D-glucopyranose) from depolymerization of holocellulose which are shown in Table 3. Aromatic and hydrocarbon compounds are considered as valuable fractions because of their contribution to the high heating value products (Mortensena et al., 2011; Gracia et al., 2013; Murata et al., 2012; Srinivasan et al., 2012). The aromatic and hydrocarbon compounds in non-catalytic cases were detected with the peak area% of only 3.58 and 8.58% respectively. The selectivity of aromatic compounds indicated the highest content of 17.27% after catalyzed by the NiCA. Significant hydrocarbon compounds were increased from 8.58% to 42.00–64.06% with the highest yield obtained by Al_2O_3 catalyst when increasing J/C ratio to 1:10. Levoglucosan and D-glucose (sugar) were not found with any catalytic testings. This result corresponds with Kaewpengkrow et.al

(2014) who reported the yields of sugar gradually reduced with increasing temperature from 400°C to 600°C and higher temperature had positive influence on the yields of pyrolytic products. It is suggested that high temperature leads to high efficiency on cracking heavy compounds from cellulose and hemicelluloses.

This result agreed well with several researchers (Kaewpengkrow et al., 2014; Lu et al., 2011) who studied the effects of pyrolysis temperature on the composition of pyrolytic products. They found that the cellulose started decomposition to form organic volatile products at pyrolysis temperature of 400°C and the levoglucosan (sugar) was favorable to form at low temperatures. Acidic structures including oleic acid, hexadecanoic acid, palmitic acid and acetic acid were also detected in bio-oil and could come from *Jatropha* oil (Kaewpengkrow et al., 2014; Murata et al., 2012). From the result, non-catalytic product contained carboxylic acid of 60.74% as main product which similar to Murata et al. (2012) who found high yield of free fatty acid (FFA of 54.3% from *Jatropha* wastes in non-catalytic pyrolysis). The CA, PdCA, and NiCA were less effective such that carboxylic acid yields were still high (19.50-31.57%) which could cause corrosion problem. The carboxylic acid fraction dropped considerably in the presence of all catalysts to 7.75-19.61% with J/C ratio of 1:5. This result is similar to Mochizuki et Al. (2013a) who reported that *Jatropha*/SiO₂ ratio of 1:5 enhanced activity in reducing the fatty acid to 7.7-17.4%, providing bio-oil with superior stability. With increasing J/C ratio to 1:10, it was found that most catalysts led to complete reduction of carboxylic acid except CA catalyst. The pH value of bio-oil is also a good indicator of its quality since low pH can lead to corrosion of the engines (Gracía et al., 2013; Murata et al., 2012; Srinivasan et al., 2012; Thangalazhy-Gopakumar et al., 2011). The pyrolytic ring scission of holocellulose produced various light products

(aldehydes, ketones, alcohols, esters). It is shown in term of the oxygenated compounds which are main responsible for the ageing reactions and instability of bio-oils (Ying et al., 2012; Pattiya et al., 2008; Lu et al., 2010)

In the presence of catalysts, volatiles released from pyrolysis process are subjected to various reactions including deoxygenation (dehydration, decarboxylation, and decarbonylation) that resulted in the production of hydrocarbons (French and Czernik, 2010). If the catalyst used for the complete deoxygenation of *Jatropha* residue is converted to hydrocarbons, the reaction can be written as Eqs. (3) which was modified from other works (Bridgwater, 1996; Kim et al., 2013).

From Table 3, the yield of aldehyde increased noticeably from 0.36% to 14.11-22.05% after catalytic reaction with J/C ratio of 1:1. The highest yielded was obtained after catalyzed by CA while PdCA and NiCA led to significant reduction of aldehyde content. In addition, oxygenated compounds presented in slight amount were ketone, alcohol and furan. It is revealed that the presence of catalysts with J/C ratio of 1:1 did not significantly reduce alcohol, aldehyde and ketone. With increasing J/C ratio to 1:5 and 1:10, aldehyde yields were almost completely reduced. The yield of furan which is toxic and may be carcinogenic, was also completely reduced with the presence of all catalysts except RuCA. The oxygenated groups were reduced from 12.94% to 5.86-16.95% and 3.96-15.50% with J/C ratio of 1:5 and 1:10, respectively. The result suggested that the oxygenated compounds were reduced by the presence of all catalysts except RuCA when compared with non-catalytic runs.

Another group of compounds that should be paid attention to was N-containing hydrocarbon compounds (N-compounds) such as N-heterocyclic and N-heteroatom

compounds. These compounds are expected since *Jatropha* wastes contain a relatively high quantity of nitrogen. N-containing compounds in liquid fuel are undesirable because they are sources of NO_x when combusted as well as corrosive nature of these substances (Kaewpengkrow et al., 2014). Total N-compounds were increased from 13.77% to 21.99-40.37% after catalytic trials. The highest N-compounds yield was obtained by Al₂O₃ catalyst. Al₂O₃ and NiCA favored the formation of N-compounds with J/C ratio of 1:5. By increasing J/C ratio to 1:10, all tested catalysts reduced N-compounds yields to less than 30%. Although with increasing J/C ratio to 1:10, N-compounds were not significantly reduced. Typically, these catalysts are not effective on reducing N-compounds. Therefore it is desirable to remove N-containing compounds prior to using these renewable biofuels through denitrogenation (HDN) reactions which is similar to the removal of N-containing compounds from petroleum feedstocks (Choudhary and Phillips, 2011). In summary increasing amount of catalysts resulted in relatively higher activity towards deoxygenation reactions which yielded low quantity of acids and oxygenated compounds, and high aliphatic and aromatic hydrocarbons.

3.2 Effect of support catalyst on pyrolytic products

In order to study how the catalyst affected the pyrolytic products, results with Al₂O₃, ZrO₂, T₁ and T₂ based catalysts were compared as shown in Fig. 1. The highest aromatic hydrocarbon content of 36.25% was obtained by T₂, followed by NiCA and PdCA. Aromatic compounds were not increased significantly by the ZrO₂ and T₁ support catalysts. The hydrocarbon yields increased with the presence in all catalysts. Application of Al₂O₃ catalyst resulted in the highest yields of hydrocarbon compounds of 64.06%, followed by RuCA and CA catalysts. Al₂O₃ and T₂ based catalysts were the most effective in which carboxylic acid could be reduced completely. Oxygenated

compounds were detected at only 3.96% and 1.58% by Al_2O_3 and T_2 catalysts, respectively. These results related to high surface area of both supports (103.38 and 204.25 m^2/g) which probably play major role on conversion of oxygenated compounds to hydrocarbons. ZrO_2 and T_1 had much lower surface area of only 12 and 4 m^2/g , respectively, which could lead to relatively high yield of oxygenated and carboxylic acid compounds. Though Al_2O_3 and T_2 increased aromatic and hydrocarbon compounds and complete elimination of acids but they also promoted N-containing compounds. Total N-containing compounds are more than 30% for Al_2O_3 and T_2 based catalysts (31.17-46.74%) which are higher than those of ZrO_2 and T_1 based catalysts (15.00-25.69%). These results are similar to several researches (Grac $\acute{\text{a}}$ et al., 2013; Mortensena et al., 2011; Murata et al., 2012; Srinivasan et al., 2012) who indicated that catalysts with high surface area displayed superior catalytic activity. In addition, the yield of sugar was completely eliminated by most catalysts except PdCT_1 and NiCT_1 . The results agree well with several researches (Ying et al., 2012; Pattiya et al., 2008; Lu et al., 2010) who found that sugar is easy to be converted by catalysts. ZrO_2 and T_1 based catalysts are less effective on deoxygenation (Lu et al., 2010). Interestingly, Pd on all supports seems to be effective on deoxygenation and production of aromatic compounds. Moreover Ni on all supports are less effective to produce N-compounds which are one advantage of this transition metal. The main N-containing compounds from catalytic pyrolysis of *Jatropha* wastes contain the N-heteroatom and N-nonheteroatom (oleonitrile, oleic acid amide, hexadecanamide and aniline). Total N-containing compounds are more than 20% for all catalysts but N-nonheteroatoms are higher for Al_2O_3 based catalysts while N-heteroatoms are higher for T_1 and T_2 based catalyst.

However N-containing compounds were mainly of N-nonheteroatom structures in which the nitrogen can possibly be removed easier than those of N-heteroatoms, and their structures are shown in previous work (Kaewpengkrow et al., 2014). Duan and Savage. (2011) also tested carbon based supporter for hydrothermal catalytic conversion of pyridine to hydrocarbons. They reported that several metal catalysts could enhance HDN reactions of pyridine during hydrothermal reactions between 250 and 400°C. The Pt/ γ -Al₂O₃ catalyst proved to be the most active for hydrothermal HDN of pyridine with main HDN products of n-butane and n-pentane while nitrogen was removed as ammonia. However, there was no report on HDN of pyrolysis oil from Jatropha. This result similar to Kim et al. (2013) who studied pyrolysis of Jatropha seedshell cake. They found that the carbon chain lengths of the pyrolytic oils are from C₁₂ to C₁₈, similar to typical diesel fuel. Nitrogen was distributed in various forms in the pyrolytic oils, owing to the fact that Jatropha seedshell cake (JSC) oil was high in amide and imide derivatives. Thus, in addition to catalytic deoxygenation, denitrogenation reaction should also be performed prior to the use of pyrolytic liquid from Jatropha waste as a quality fuel feedstock (Kaewpengkrow et al., 2014; Kim et al., 2013).

Generally, bio-oil contains some heavy aromatic compounds while gasoline and diesel include mixtures of hydrocarbons with relatively low chain lengths of 5–10 and 12–20, respectively (Bulushev and Ross, 2011). From the result, the major compounds were aliphatic hydrocarbons which were presented by the carbon range of C₅–C₁₁, C₁₂–C₂₀ and > C₂₀ as shown in Fig. 2. The main hydrocarbons are 1-Octene, 1-heptene, 1,3,5-cycloheptatriene and 1-heptadecene. High yields of C₅–C₁₁ (30.04-48.10%) was achieved with the presence of catalyst in Al₂O₃ based catalysts, which are suitable as gasoline. It might be due to larger surface area of Al₂O₃ than other catalysts. Similarly,

high yields of C_{12} - C_{20} were obtained at 35.80% by PdCT₁ which are suitable as diesel fuel. The result indicated that these catalysts were effective for deoxygenation of the pyrolysis vapors to form hydrocarbons for quality biofuels. However the yields of long chain hydrocarbon ($>C_{20}$) were only 0.42-2.26%. Similar behavior was also observed during the catalytic fast pyrolysis by other researchers as shown in Table 4. Previous catalytic pyrolysis studies with different types and amounts of catalysts resulted in the oxygenated compound yields of around 20-60%. It can be concluded that these catalysts were more effective on cracking large molecules of hydrocarbon into light hydrocarbon than other support catalysts, although their surface area are lower than other catalysts. Other studies reported a reduction in oxygenated compounds and the presence of large amounts of polycyclic aromatic hydrocarbons (PAHs) during the catalytic pyrolysis reaction (Gracia et al., 2013; Murata et al., 2012; Srinivasan et al., 2012).

PAHs deserve more attention due to their toxicity in the environment and potential role in the incidence of cancer (Kaewpengkrow et al., 2014; Qiang et al., 2009). The presence of PAHs in transportation fuel may result in possible emission by attachment to particulate matter in the exhaust from automobiles. Therefore, the proper catalyst for the catalytic pyrolysis to convert *Jatropha* wastes into bio-fuel should not only promote the monocyclic aromatic hydrocarbons (MAHs) but also inhibit the formation of coke and PAHs (Mochizuki et al., 2013b). Among the hydrocarbon compounds, heptene, octene, and heptadecene were primary compounds. Other alkyl aromatics such as toluene, xylene, and ethylbenzene were also seen in the products. PAH such as naphthalene was detected only 1-2% with the presence of all catalyst.

The inclusion of oxygenated compound is one of the most important problems of bio-oil utilization which led to low-quality and short shelf life fuel. Accordingly,

reduction of oxygen content is one of the primary aims of this study. The result showed that all catalysts led to the decrease in oxygenated species from 73.68% to less than 40% in all supporter except CZ catalyst. It can be suggested that the oxygenated compounds can diffuse into the pores of the catalyst and result in hydrocarbon compound formation through decarbonylation, dehydration, and deoxygenation reactions (Vichaphund et al., 2014a, 2014b). In the presence of catalyst, high total hydrocarbon compounds were obtained by T₂, CA, NiCA, and Al₂O₃ catalysts, respectively. The effect of various catalysts on the oxygenated compounds and total hydrocarbon is shown in Fig. 3. These catalysts exhibited improved selectivity toward the aromatic and hydrocarbon production of more than 60% and decreased oxygenated compounds to less than 10%. Thus, it can be concluded that these catalysts are relatively suitable for decreasing the amount of oxygenated compounds and providing bio-oil with enhanced stability. Finally, it can be noticed that these catalyst supports displayed relatively high activity towards deoxygenation reactions which resulted in low quantity of acids and other oxygenated compounds, and produced high aromatic and hydrocarbon compounds. Generally, high J/C ratio had positive influence on low yields of oxygenated compounds and high yields of hydrocarbon compounds. Among twenty catalysts tested, the presence of T₂ catalysts displayed the highest yield of aromatic hydrocarbons (36.25%), relatively high hydrocarbons (38.07%), low oxygenated compounds (0.65%) and no carboxylic acid contents. On the other hand, Al₂O₃, CA and RuCA presented higher yields of aliphatic hydrocarbon compounds of 64.06%, 55.92%, and 56.62%, respectively. Total hydrocarbon compounds from T₂, CA, Al₂O₃, and RuCA were 74.32%, 67.14%, 65.81%, and 62.49%, respectively, while oxygenated compounds were in the range of 3.96-43.70%. The result showed that Al₂O₃ and T₂

based catalysts reduced oxygenated yields to less than 20% while oxygenated yields of ZrO_2 and T_1 were yet higher than 30%. However yields from these catalysts contained considerable amount of N-containing compounds (24.06-49.27%) implying that additional denitrogenation is further required. It may be suggested that these catalysts were effective for cracking large molecules of the pyrolysis vapors and possibly be applied to improve properties of pyrolytic product vapors from *Jatropha* wastes.

4. Conclusions

Upgrading of vapors from *Jatropha* pyrolysis using Py-GC/MS with Al_2O_3 based catalysts completely eliminated carboxylic acids and significantly increased hydrocarbons (J/C of 1:10). Aromatic and hydrocarbon yields increased in the order of $\text{T}_2 > \text{Al}_2\text{O}_3 > \text{CA} > \text{NiCA} > \text{RuCA}$. Aliphatics ($\text{C}_5\text{-C}_{11}$) was the main hydrocarbons in the presence of Al_2O_3 based catalysts, suggesting that they were effective for cracking large molecules of the pyrolysis vapors and may possibly be applied to improve the properties of pyrolytic products vapors from *Jatropha* wastes. Al_2O_3 and T_2 supports were the most effective in term of increased aromatics and hydrocarbons and decreased oxygenated compounds but they also promoted N-containing compounds.

5. Acknowledgement

This research has been supported by National Research University Project, Office of High Education Commission (WCU-042-EN-57). Authors would also like to thank the National Metal and Materials Technology Center, Thailand (Project No.MT-B-53-END-07-082-C). The Py-GC/MS system was supported by JST/JICA, Science and Technology Research Partnership for Sustainable Development (SATREPS), Japan. P. Kaewpengkrow also appreciates the scholarship provided by the Thailand Graduate

6. References

1. Abdul Khalil, H.P.S., Sri Aprilia, N.A., Bhat, A.H., Jawaid, M., Paridah, M.T., Rudi, D., 2013. A Jatropha biomass as renewable materials for biocomposites and its applications. *Renewable and Sustainable Energy Reviews*. 22, 667-685.
2. ASTM E871, 2006. Standard Test Method for Moisture Analysis of Particulate Wood Fuels, ASTM International, West Conshohocken, PA.
3. ASTM E872, 2006. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels, ASTM International, West Conshohocken, PA.
4. ASTM D1102, 2007. Standard Test Method for Ash in Wood, ASTM International, West Conshohocken, PA.
5. ASTM D240, 2009. Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter, ASTM International, West Conshohocken, PA.
6. Bridgwater, A., 1996. Thermal Biomass Conversion and Utilization–Biomass Information System, Research and Development, European Commission – Science, Luxembourg.
7. Bulushev, D.A., and Ross, J.R.H., 2011. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review. *Catalysis Today*. 171, 1–13.
8. Choudhary, T.V., and Phillips C.B., 2011. Renewable fuels via catalytic hydrodeoxygenation. *Applied Catalysis A: General*. 39, 1–12.

9. Duan, P., and Savage, P.E., 2011. Catalytic hydrothermal hydrodenitrogenation of pyridine. *Applied Catalysis B: Environmental*. 108-109, 54-60.
10. French, R., and Czernik, S., 2010. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process Technology*. 91, 25-32.
11. Grac $\square$ a, I., Lopes, J., Cerqueira H.S., Ribeiro M.F., 2013. Bio-oils Upgrading for Second Generation Biofuels. *Ind. Eng. Chem. Res.* 52, 275-287.
12. Iojoiu, E.E., Domine, M.E., Davidian, T., Guilhaume, N., Mirodatos, C., 2007. Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia. *Applied Catalysis A: General*. 323, 147-161.
13. Kaewpengkrow, P., Atong, D., Sricharoenchaikul, V., 2014. Effect of Pd, Ru, Ni and ceramic supports on selective deoxygenation and hydrogenation of fast pyrolysis Jatropha residue vapors. *Renewable Energy*. 65, 92-101.
14. Kim, S.W., Koo, B.S., Ryu, J. W., Lee, J.S., Kim C.J., Lee, D. H., Kim, G.R., Choi, S., 2013. Bio-oil from the pyrolysis of palm and Jatropha wastes in a fluidized bed. *Fuel Processing Technology*. 108, 118-124.
15. Lu, Q., Zhang, Y., Tang, Z., Li, W.Z., Zhu, X.f., 2010. Catalytic upgrading of biomass fast pyrolysis vapors with titania and zirconia/titania based catalysts. *Fuel*. 89, 2096-2103.
16. Lu Q. Yang, X., Dong, C., Zhang, Z., Zhang, X., Zhu, X., 2011. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: analytical Py-GC/MS study. *Journal of Analytical and Applied Pyrolysis*. 92, 430-438.
17. Mochizuki, T., Atong, D., Chen, S-Y., Toba, M., Yoshimura, Y., 2013. Effect of SiO₂ pore size on catalytic fast pyrolysis of Jatropha residues by using pyrolyzer-

GC/MS, Catalysis Communications. 36, 1–4.

18. Mochizuki, T., Chen, S-Y., Toba, M., Yoshimura, Y., 2013. Pyrolyzer–GC/MS system-based analysis of the effects of zeolite catalysts on the fast pyrolysis of Jatropha husk. *Applied Catalysis A: General*. 456, 174– 181.
19. Mortensen, P.M., Grunwaldt, J.D., Jensen, P.A., Knudsen, K.G., Jensen, A.D., 2011. Review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*. 407, 1– 19.
20. Murata, K., Liu, Y., Inaba, M., Takahara, I., 2012. Catalytic fast pyrolysis of jatropha wastes. *J. Anal. Appl. Pyrolysis*. 94, 75-82.
21. Pattiya, A., Titiloye J.O., Bridgwater, A.V., 2008. Fast pyrolysis of cassava rhizome in the presence of catalysts. *J. Anal. Appl. Pyrolysis*. 81, 72–79.
22. Qiang, L., Wen-zhi, L., Dong, Z., Xi-feng, Z., 2009. Analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) of sawdust with Al/SBA-15 catalysts. *J. Anal. Appl. Pyrolysis*. 84, 131– 138.
23. Srinivasan, V., Adhikari, S., Chattanathan, S.A., Park, S., 2012. Catalytic Pyrolysis of Torrefied Biomass for Hydrocarbons Production. *Energy Fuels*. 26, 7347–7353.
24. TAPPI T203, 1999. Alpha-, Beta- and Gamma-Cellulose in Pulp, Technical Association of the Pulp and Paper Industry, Norcross, GA.
25. TAPPI T222, 2006. Acid-Insoluble Lignin in Wood and Pulp, Technical Association of the Pulp and Paper Industry, Norcross, GA.
26. Thangalazhy-Gopakumar, S., Adhikari, S., Gupta, R.B., Tu M., Taylor, S., 2011. Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments. *Bioresource Technology*. 102, 6742–6749.

27. Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., Atong, D., 2014. Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Renewable Energy*. 65, 70-77.
28. Vichaphund, S., Aht-Ong, D., Sricharoenchaikul, V., Atong, D., 2014. Characteristic of fly ash derived-zeolite and its catalytic performance for fast pyrolysis of Jatropha waste. *Environmental Technology*. DOI: 10.1080/09593330.2014.900118
29. Ying, X., Tiejun, W., Longlong, M., Guanyi, C., 2012. Upgrading of fast pyrolysis liquid fuel from biomass over Ru/c-Al₂O₃ catalyst. *Energy Conversion and Management*. 55, 172–177.
30. Zhang, H., Xiao, R., Jin, B., Xiao, G., Chen, R., 2013. Biomass catalytic pyrolysis to produce olefins and aromatics with a physically mixed catalyst. *Bioresource Technology*. 140, 256–262.

Fig. 1. Average total compositional wt% of pyrolytic products with various supported catalysts with J/C ratio of 1:10

Fig. 2. Hydrocarbon compounds selectivity for fast pyrolysis of Jatropha wastes with various catalysts

Fig. 3. Effect of various catalysts on oxygenated compounds and total hydrocarbon compounds of pyrolytic products

Table 1 Comparison between characteristics of Jatropha waste and other biomass

Table 2 Physical properties of metal catalysts

Table 3 Pyrolytic products from Py-GC/MS of Jatropha waste at 600°C with and without Al₂O₃ based catalysts

Table 4 Comparison of the product selectivity from catalytic fast pyrolysis vapors of biomass

Table 1 Comparison between characteristics of Jatropha waste and other biomass

Biomass feedstock	This work ^a	JSC ^b	JR ^c	Cedar ^c	Pine wood ^d	Rice stalk ^e
Proximate analysis (wt.%)						
Volatile	73.80	79.80	-	-	-	66.3
Fixed carbon	13.60	14.13	-	-	-	16.3
Moisture	6.80	2.56	-	-	5.6	3.0
Ash	5.80	3.42	-	-	0.9	14.5
Elemental analysis (wt.%)						
C	44.35	50.52	48.0	50.0	45.7	35.4
H	6.76	6.15	5.8	6.1	6.5	4.8
O	32.95	39.41	45.2	-	45.5	44.4
N	7.35	2.32	1.6	0.1	0.1	1.0
S	0.47	-	1.3	-	-	-
Other*	8.12	-	-	-	-	-
Component analysis (wt.%)						
Cellulose	18.00	36.64	26.2	34.2	43.8	-
Hemicellulose	59.20	4.82	16.2	15.3	19.9	-
Lignin	22.80	39.61	20.2	32.1	24.3	-
Other	n/a	18.94	23.1	4.8	-	-
HHV (MJ/kg)	18.83	20.80	-	-	-	-

^aKaewpengkrow et al., 2014, ^bKim et al., 2013, ^cMochizuki et.al., 2013, ^dThangalazhy-Gopakumar et al., 2011,

^eZhang et al., 2013, *By difference

Table 2 Physical properties of metal catalysts

Catalysts	Surface area (m ² /g) †	Particle size (µm)*	Actual metal loading (EDS, %)	Catalysts	Surface area (m ² /g) †	Particle size (µm)*	Actual metal loading (EDS, %)
Al ₂ O ₃ (A)	103.38	11.76**	-	TiO ₂ (T ₁)	4.15	8.51	-
CA	90.35	65.89	7.3	CT ₁	3.40	3.52	-
PdCA	89.93	27.94	1.19	PdCT ₁	3.57	4.31	0.81
RuCA	85.91	30.73	1.68	RuCT ₁	3.48	3.75	0.21
NiCA	87.91	30.96	1.07	NiCT ₁	3.29	3.69	0.82
ZrO ₂ (Z)	12.78	11.80	-	TiO ₂ (T ₂)	204.25	0.51	-
CZ	11.83	10.25	-	CT ₂	45.91	0.50	-
PdCZ	12.37	10.46	1.69	PdCT ₂	40.72	0.54	0.77
RuCZ	10.49	10.20	2.01	RuCT ₂	35.18	0.54	1.32
NiCZ	11.61	9.84	1.64	NiCT ₂	33.34	0.53	0.84

* Mastersizer-S Version 2.19, Malvern Instruments Ltd., UK, ** nm

† Autosorb-1 Version 1.19, Quantachrome Corporation, USA.

Table 3 Pyrolytic products from Py-GC/MS of Jatropha waste at 600°C with and without Al₂O₃ based catalysts

Catalyst	J : C ratio	Hydrocarbon		Oxygenated compounds							N-compounds		
		Aliphatic	Aromatic	Phenol	Alcohol	Aldehyde	Ester	Ether	Furan	Ketone	acid	N-compounds	Sugar
None	1:0	8.58	3.58	3.88	2.21	0.36	0.62	0.00	1.04	4.83	60.74	13.77	0.00
Al ₂ O ₃	1:1	23.38	7.31	2.37	0.00	14.11	11.39	0.00	1.17	0.86	6.48	31.56	0.00
CA		12.56	5.82	2.67	1.05	22.05	7.85	0.00	1.70	0.63	19.50	26.19	0.00
PdCA		12.99	7.26	3.18	2.35	0.00	1.57	0.00	1.41	5.04	30.46	28.13	0.00
RuCA		22.08	7.20	4.52	1.68	16.21	8.86	0.00	0.00	4.29	5.71	29.48	0.00
NiCA		13.17	4.56	2.37	2.32	0.00	10.70	0.00	1.82	3.84	31.57	22.35	0.00
Al ₂ O ₃	1:5	36.67	10.05	0.00	2.80	4.82	3.46	0.00	0.66	0.75	0.00	40.37	0.00
CA		34.34	9.56	2.05	0.00	3.26	8.53	0.00	0.00	0.00	8.40	33.88	0.00
PdCA		26.49	16.80	2.67	1.65	0.00	11.66	0.00	0.00	0.97	7.75	32.03	0.00
RuCA		25.86	8.15	1.49	1.73	1.56	8.21	0.00	0.00	0.00	19.61	31.17	0.00
NiCA		40.60	8.96	1.87	0.50	2.00	1.49	0.00	0.00	0.00	6.63	36.14	0.00
Al ₂ O ₃	1:10	64.06	1.75	0.00	0.63	2.50	0.00	0.00	0.00	0.83	0.00	29.64	0.00
CA		55.92	11.22	0.00	5.04	1.84	0.00	0.00	0.00	0.00	0.76	25.24	0.00
PdCA		42.00	17.16	0.00	0.00	0.64	3.27	5.14	0.00	2.23	0.00	29.53	0.00
RuCA		56.62	5.87	2.67	0.00	3.20	7.43	0.00	0.94	1.26	0.00	21.99	0.00
NiCA		48.93	17.27	0.00	5.28	2.16	0.00	0.00	0.00	2.42	0.00	23.95	0.00

Table 4 Comparison of the product selectivity from catalytic fast pyrolysis vapors of biomass

Type of catalyst	Biomass to catalyst ratio	Pyrolysis product (% peak area)			References
		Aromatic	Hydrocarbon	Oxygenated	
Zeolite (Microporous)					
H-ZSM-5	1:4, 1:9	7.4-42.5	-	-	Thangalazhy-Gopakumar et al., 2011
ZSM-5	1:5, 1:10	-	16	-	French and Czernik, 2010
SiO ₂	1:1, 1:5	2.7-5.3	7.3-18.1	> 40	Mochizuki et al., 2013a
H-USY, H-Beta, H-Mordenite, H-ZSM-5	1:1,1:5	-	2.2-50.7	12-60	Mochizuki et al., 2013b
Catalyst (Mesoporous)					
ZrO ₂ , TiO ₂	1:2	-	0.1-13.1	-	Lu et al., 2010
Al ₂ O ₃ , ZrO ₂	1:1, 1:5	1.0-17.0	15.0-40.0	20-40	Kaewpengkrow et al., 2014
Al ₂ O ₃ , ZrO ₂ , TiO ₂	1:1, 1:5, 1:10	2.3-17.3	20.0-64.0	5-30	This work

Fig. 1. Average total compositional wt% of pyrolytic products with various supported catalysts with J/C ratio of 1:10

Fig. 2. Hydrocarbon compounds selectivity for fast pyrolysis of Jatropha wastes with various catalysts

Fig. 3. Effect of various catalysts on oxygenated compounds and total hydrocarbon compounds of pyrolytic products