Evaluation of Ni-based catalysts for the catalytic fast pyrolysis of Jatropha residues

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Fast pyrolysis with cheap Ni-based catalysts was evaluated to produce bio-oil from jatropha residues. By Py-GC/MS method with catalyst/jatropha weight ratio of 6.2, Ni/zeolite-based catalysts such as NiMo(O)/Y(14) were found to be promising candidates for total hydrocarbon formations. But, with low catalyst/jatropha ratio of 0.35-0.76, the total hydrocarbon selectivities were NiMo(O)/Y(14)(71.7%) > PtPd/ZSM(38)(68.8%) > Ni2P/Y(14)(65.4%) > NiMo(O)/Beta(27)(63.9%) > NiMo(O)/ZSM(38)(60.1%) > none (36.4%), when the pyrolysis was carried out using a stainless-steel reactor under N₂ gas flow. When jatropha residues (50g) was used with NiMo(O)/Y(14) at 500 °C, total liquid yield was as high as 49.9%, including 21.3% of organic liquid. Taking into account higher **Aromatic/Aliphatic** selectivities, lower acid selectivities at both 600 °C and 500 °C, Ni-based catalysts such as NiMo(O)/Y(14) were found to be effective and comparable to PtPd/ZSM(38). The acid values of organic liquids obtained at 600 °C were 2.74-7.02 mg-KOH.kg⁻¹, being much lower than 28.2 mg-KOH.kg⁻¹ in the absence of catalyst. The estimated higher heating values (HHV) of the liquid were 32-33 MJ/kg. The NiMo(O)/Y(14), NiMo(O)/ZSM(38) and Ni2P/Y(14) catalysts could be regenerated by calcination at 600 °C, followed by subsequent hydrogenation, and the organic liquid product yields remained constant at fresh and regenerated catalysts and **total hydrocarbon selectivities were also constant within the experimental error**. Thus, under these pyrolysis conditions, Ni-based catalysts seems to be better and cheaper candidates than PtPd systems.

KEYWORDS. Fast pyrolysis, Jatropha residues, Ni-based Catalyst, Liquid hydrocarbon properties

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Due to the advantages of being CO₂ neutral, having low sulfur content compared to petroleum fuels, and being easy to transport, renewable biomass-based liquid fuels will become more important in the future as partial alternatives to fossil fuels. In particular, technology that can convert biomass wastes to valuable liquid fuels and chemicals will be important for solving our energy and environmental problems. In general, gasification and fermentation are used for biomass conversion. Gasification needs very high temperature of 900-1000 °C and subsequent liquefaction processes of biogas such as Fischer-tropsch reaction and methanol synthesis are required for obtaining liquid fuel [1]. Fermentation proceeds at mild conditions, but slow productivity, pretreatment of biomass and fermentation wastes are still problem to be solved to save more energy.

Pyrolysis is one of a thermochemical process that is an efficient way of converting biomass into liquids (bio-oil) with gases and char at temperature as relatively low as 300 °C-600 °C. In particular, fast pyrolysis process of biomass materials is effective for raising liquid product yield [2]. In order to raise liquid product yields in the pyrolysis, parameters such as temperature, heating rate, residence time, pressure, and catalyst, biomass type and characteristics (particle size, shape, and structure), are extremely important [3]. This technology would be economical on the smaller scale where smaller distributed plants can be built close to the location of the biomass [4]. However, the bio-oils are of poor quality. They are thermally unstable, degrade with time, acidic, have a low heating value, and oxygen content is 40-45 %, therefore, these liquids have not a drop-in quality compatible with existing petroleum-derived oils [5] and, therefore, bio-oils have to be catalytically upgraded [6-8].

In recent years, *Jatropha* plant has been widely gaining attentions as a potential renewable energy crop in which its extracted oil has similar properties to that of palm oil [9]. 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 after oil extraction undergo fast pyrolysis, by which the wastes can be directly converted 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 may be upgraded to be used as a liquid transportation fuel [10]. If *Jatropha* residues can be effectively converted to drop-in liquid product with *in situ* upgrading, the *Jatropha* plant would become an economically valuable alternative source of biofuels [11].

Upgrading 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 [12], but these reactions need high H₂ pressure. Consequently, *in situ* upgrading of bio-oil by catalytic reforming of pyrolytic vapors product would require catalysts effective under atmospheric pressure. 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 [10, 13-16] which are effective to convert the highly oxygenated compounds to aromatic hydrocarbons. We studied fast pyrolysis of *Jatropha* wastes and the result showed that aromatics are largely formed above 90% of overall GC peak area by using catalysts (H-ZSM-5 and zeolites) [13]. Zhang et al. [17] added mesoporous catalysts (c-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%.

Recently, metal-modified zeolites are utilized for deoxygenated reactions which were reported by several researches [18-21]. **Very recently, it has been reported that aromatic hydrocarbon selectivity was 91% using metal-modified H-ZSM-5 by Py-GC/MS methods, where biomass/catalyst ratio is 1/10 [22].** We have already reported PtPd-modified zeolite catalysts for fast pyrolysis of *Jatropha* wastes [23], but these noble metals are extremely expensive and may not be suitable from industrial point of view. Thus, the purpose of this paper is to explore Ni-based zeolite catalysts comparable to PtPd-modified zeolites,

with respect to the selectivities of aromatic and aliphatic hydrocarbon, formed by deoxygenation.

2. Materials and methods

2.1 Materials.

Jatropha wastes were obtained from Bioenergy development Co.,Ltd., Thailand. The wastes were sieved to obtain five fractions between 0.5 mm and 5 mm, where 0.5-1.0 mm, 1.0-1.5 mm, 1.5-2.0mm, 2.0-3.3mm and 3.3-5.0mm were used and mixtures of the five fractions were employed as a five-gram portion. Pellet-type microporous materials such as H-ZSM-5, USY and Beta were purchased from Tosoh Corp. The zeolite name and Si/Al₂ ratio are abbreviated as ZSM(38), Y(14), and Beta(27). Ni(NO₃)₂·6H₂O, (NH₄)₃PO₄·3H₂O and (NH₄)₆MoO₂₄·4H₂O, Pt(NH₃)₄Cl₂·H₂O and Pd(NO₂)₂(NH₃)₃ were purchased from Wako Chemicals, Japan and Soekawa Chemical. The metal-modified zeolite catalyst used in this study was prepared by impregnating zeolite support with Ni(NO₃)₂·6H₂O and (NH₄)₆MoO₂₄·4H₂O, followed by drying at 100 °C and calcination for 5 h at 600 °C. The NiMo/ZSM(38) catalyst was pre-reduced in an autoclave at 500 °C for 5 h under a 4 MPa hydrogen atmosphere. The obtained catalyst is abbreviated as NiMo(O)/ZSM(38). Similar processes were performed for the preparation of Ni₂P-based catalysts [24], where Ni(NO₃)₂·6H₂O and (NH₄)₃PO₄·3H₂O were used and supports were ZSM(38), Y(14), Beta(27), ZrO₂ and SiO₂. The calcination and reduction temperatures were 500 °C.

In NiMo(S)/Y(14), after drying at 100°C, the catalyst precursor was treated with (NH₄)₂S, followed by N₂ gas treatment at 450 °C for 10 h. The PtPd/ZSM(38) was prepared by immersion impregnation of ZSM(38) with Pt(NH₃)₄Cl₂·H₂O and Pd(NO₂)₂(NH₃)₃, followed by drying at 100 °C and calcination for 5 h at 500 °C. The PtPd/ZSM(38) catalyst was pre-reduced in an autoclave at 250°C for 5 h under a 4 MPa hydrogen atmosphere. NiMo-based catalysts were pre-reduced in an autoclave at 500 °C for 5h under 4MPa hydrogen, while Ni₂P-based catalysts were reduced at 500°C for 3h under an atmospheric pressure of hydrogen.

2.2 Analysis.

Proximate and ultimate analyses were briefly performed using thermogravimetric analysis (TGA) and elemental analysis methods. Moisture and volatile content were obtained from TGA analysis and the fixed carbon content was calculated by difference. TGA was performed in nitrogen using a TG 2000 (Bruker AXS). Approximately 10 mg of sample was heated from 40 °C to 800 °C at a typical ramp rate of 20 °C/min in a total flow rate of 50 ml/min. The moisture content was considered to account for the weight loss when the sample was heated up to 160°C. Two step devolatilization began after the temperature reached 160°C and was completed at 600°C. TGA pyrolysis showed a gradual loss in mass above 600°C which can be attributed to volatile metal loss and carbonate decomposition. Argon gas was used for a proximate analysis of Jatropha wastes, while air flow was used for deposit carbon combustion of used catalysts. The C, H, N contents were measured using elemental analysis methods, where CE INSTRUMENTS EA1110 was used and all measurements were repeated in triplicate and a mean value is reported. The data are summarized as proximate and ultimate analysis in **table 1**. BET surface area, total pore volume (V_p), and mean pore diameter (dp) of all catalysts were determined by N₂-physisorption using a BELSORP MAX apparatus (Microtrac BELL Co. Ltd.) at liquid-N₂ temperature. V_p and dp were estimated by the Barrett–Joyner–Halenda (BJH) method [25]. The Ni particle size of the reduced metal particle was measured by CO chemisorption method, which was carried out by using the BEL-CAT apparatus. Before chemisorption of CO, the catalysts (50 mg) were pretreated in He for 35 min and then reduced for 30 min in a 5% H₂/Ar gas flow of 50 ml/min and in He for 15 min at 400 °C in a reaction chamber. After this pretreatment, the samples were cooled down at 50 °C under He gas flow and CO pulse measurements were carried out using 10% CO/He gas flow of 50 ml/min. Finally, particle size of each metal was determined from CO pulse data. For comparison,

particle size of Mo is estimated, based on the assumption that Ni and Mo are independently present on the support.

The reducibility of three typical prepared catalysts was studied by H₂-temperature-programmed reduction (TPR) using the BEL-CAT apparatus. Before the analysis, 50 mg of sample in a quartz tube was purged with He at 200 °C for 1 h in order to remove the impurities on the surface of the catalyst. After the sample was cooled to room temperature in flowing He, TPR measurements were carried out using 5% H₂/Ar (v/v) mixture with a flow rate of 30 ml/min at a heating rate of 5°C/min from room temperature to 800 °C and the H₂ consumption was recorded with a TCD.

2.3 Pyrolysis.

In order to compare product distributions of volatile matter in the absence and presence of catalyst, Pyro-GC/MS analysis was performed on a PY-2020iS pyrolyser (Frontier Lab) connected to an Agilent model 7890A gas chromatograph (GC) interfaced with an Agilent model 5975C mass spectrometer (MS). Jatropha wastes were sieved prior to use. Samples of 0.4 mg in holder were rapidly pyrolyzed at 600 °C by dropping the sample holder into furnace. When catalyst was used, the catalyst to waste sample ratio was 6.25, **which was the same as our previous conditions [13]** and these reactants were prepared by physically mixing the waste and the catalyst. The products were separated on an Ultra alloy DX-30 30 m capillary column, 0.25 i.d., 0.15 mm film thickness. The GC oven was programmed with the following temperature regime: hold at 50 °C for 1 min, ramp to 400 °C at 20 °C/min, hold at 400 °C for 15 min. Product selectivities were evaluated by area percentage (%) of each peak detectable in GC/MS.

Pyrolysis experiments were independently carried out using a stainless-steel tube (6 cm diameter and 40 cm long) with two-types of trap (ice and liquid N₂) and plastic gas reservoir. Prior to pyrolysis reaction, the tablet-type catalyst (10 g) was introduced into the tube and pre-heated to 600 °C under N₂ flow of 2000 ml.min⁻¹. **Then, total 30 g of the waste material with each five gram portion was dropped six times** to the tube immediately and gaseous and liquid products were collected to traps and plastic gas reservoir. **Total reaction time was 30 min.** Then, these gaseous and liquid products were analyzed by off-line FID and TCD gas chromatographies. For gaseous products, Porapak Q and MS 5A columns for the TCD were used. And also FID analysis of gaseous product was performed using KCl-PLOT column. Liquid products were collected without solvent and organic phase was analyzed by two FID-GCs, where UA-DX30 and UA-CW columns were used. For FID analysis, dioxane was used as internal standard. The each carbon selectivity is defined as the moles of carbon in each product divided by the total carbon in the feed. The amount of total carbon initially introduced was estimated by elemental analysis and the amount of carbon deposit over the catalyst surface was analyzed by thermo-gravimetric analysis under air conditions. The acid value of the liquid product was measured with an automatically operated titration apparatus Methrom 905 Titrand. Approximately 0.1 g of liquid products was dispersed in toluene media. The KOH titrant was employed into the media with constant volume. The acid values were determined using the amount of KOH at equivalent point. The amount of C, H, N and O was estimated by elemental analysis of bio-oil (organic phase). The higher heating values (HHV) were estimated by Dulong equation [26]. The amount of N and S were characterized by nitrogen and sulfur detector that directly connect with TS-100V trace sulfur analyzer (Mitsubishi Chemical Corporation).

To study the efficiency of the catalyst, the used catalysts after reaction were regenerated as follows. Used catalyst covered with carbon was calcined at 600°C for 5 h with a heating rate of 4°C/min followed by reduction at 250°C for 5 h in an autoclave under a 4 MPa hydrogen atmosphere.

3. Results and Discussion

3.1 Catalyst properties

Particle size and textural properties, such as BET surface area, pore volume (Vp), and pore diameter (dp), of the catalysts are given in Table 2. The Ni and Mo loading were 10 wt% and 30 wt% and usually actual Ni loading would be consistent with initial Ni loading [27]. The particle sizes of Ni (8.42-25.1 nm) on the support surface of the NiMo catalysts were smaller than those of Mo (20.9-62.2 nm). The Ni particle sizes of Ni₂P on the porous supports were 36.5-49.0 nm, being larger than those of NiMo catalysts. Surface area, pore volume, and pore diameter of these catalysts were 176.0-464.5 m²g⁻¹, 0.098-0.286 cm³g⁻¹, and 1.50-11.5 nm, respectively. In these cases, both Vp and dp were estimated by the BJH methods. The dp value of ZSM(30) was 2.58 nm. The Surface areas of Ni₂P/ZrO₂ and Ni₂P/SiO₂ (35.1 and 63.7 m²g⁻¹) were smaller than other porous support catalysts.

Figure 1 shows TPR profiles of three NiMo(O)/zeolite supports, which have three broad reduction peaks between 400 °C and 700 °C. The peak at 494 °C can be assigned to a partial reduction step of molybdenum trioxide (Mo⁶⁺ → Mo⁴⁺) of amorphous, multilayered Mo oxides or octahedral Mo species [28]. The peak at 555 °C can be related to NiMoO₄-like phase [29], while the peak at 627 °C may be due to the intermediate-reducible of orthorhombic MoO₃ [30-31]. Two peaks at 494 °C and 555 °C were detected for these three catalysts. The peak at 627 °C was clear for NiMo(O)/Beta(27), while the peak was not clear for NiMo(O)/ZSM(38) and NiMo(O)/Y(14) catalysts. High temperature (HT) peak between 700 °C and 900 °C may be generally ascribed to a deep reduction of all Mo species including less reducible tetrahedral Mo⁶⁺ species or bulk MoO₃ [32], but the HT peak was not clear below 800 °C for three catalysts.

3.2 Fast pyrolysis of jatropha residues using Py-GC/MS.

The catalytic fast pyrolysis of jatropha residues was carried out using Ni-based catalysts. Table S1 shows the product selectivity as estimated by Py-GC/MS analysis at 600 °C, by measuring the relative peak area % of liquid products. The carbon mass balance remained unknown, since gaseous and solid products were not measured. In this case, gaseous products contained C₂-C₄ hydrocarbons as well as CH₄, CO, and CO₂. The distribution of compounds in bio-oils was determined using a semi-quantitative study based on the percentage area of the chromatographic peaks. Compounds were identified using a combination of a mass spectral database and retention data for standard components. Analysis of bio-oil products indicated the production of a range of aromatic hydrocarbons (1.Aromatic), aliphatic hydrocarbons (2.Aliphatic), phenols (3.Phenol), oxygenates (4.Oxy, alcohols + ketones + ethers), acids and esters (5.Acid) and nitrogen-containing compounds (6.N-comp.) and others (7.Others). The Aromatic included, typically, benzene, toluene, xylenes, methylindene, naphthalene, and methyl-naphthalenes. The Aliphatic included, typically, decene, pentadecane, hexadecene. The Phenol included phenol and methylphenol. The Oxy products contained benzenepropanal, benzofuran. The acids and esters contained hexadecanoic acid, octadecenoic acid (oleic acid), and octadecanoic acid (stearic acid) [33]. The N-comp. included typically benzylnitrile, indole, methylindole, hexadecanenitrile. Of these products, particular attention would be given to acid selectivities as well as aromatic and aliphatic hydrocarbons.

In the absence of a catalyst, fast pyrolysis of jatropha residues resulted in the major fraction consisting of 96.1% of Acid and 2.16% of Oxy with small amount of Aromatic and Aliphatic. Addition of Ni-based catalysts significantly changed the product distribution. The proportions of Aromatic and Aliphatic compounds increased, whereas Acid compounds were greatly reduced. Total selectivities of Aromatic and Aliphatic of effective Ni-based catalysts such as NiMo(O)/ZSM(38), NiMo(O)/Y(14), Ni₂P/Beta(27) and NiMo(O)/Beta(27) were 78.2%-45.7%, being comparable with PtPd/ZSM(38)(97.3%), as shown in Table S1 in detail. Acid selectivities were PtPd/ZSM(38)(0%) <

NiMo(O)/ZSM(38) (1.6%) < NiMo(O)/Y(14) (3.4%) < NiMo(O)/Beta(27) (16.5%) < Ni2P/Y(14) (36.2%). An aim of this research is to explore an excellent Ni catalyst. So, from Py-GC/MS methods, we expect that NiMo(O)/ZSM(38), NiMo(O)/Y(14), Ni2P/Beta(27) (49.6%) and NiMo(O)/Beta(27) are promising candidates and next, the effects of reaction temperature and weight ratio of catalyst to jatropha residues are examined using these four catalysts. (See Table S1 in detail).

As shown in Fig.2(a), with NiMo(O)/ZSM(38), both Aromatic and Aliphatic selectivities were roughly constant at 64.9%-82.4%, and 26.7%-30.3% with the increase in the reaction temperature from 500-600 °C. The Acid selectivities were 0.4%-1.8%. Total selectivities of Aromatic and Aliphatic increased from 58.4% to 79.6%, with the increase in the weight ratio of catalyst to jatropha residues from 4 to 10, while the Acid selectivities decreased from 3.6% to 0%. As shown in Fig.2(b), with NiMo(O)/Beta(27), total Aromatic and Aliphatic selectivities were roughly 34.7-69.5% at 500-600 °C, and the acids were 2.4-47%. Total selectivities of Aromatic and Aliphatic increased from 32.6% to 71.0%, with the increase in the weight ratio of catalyst to jatropha residues from 4 to 10, while the Acid selectivities decreased from 28.5% to 0%. As shown in Fig.2(c), with NiMo(O)/Y(14), total Aromatic and Aliphatic selectivities were roughly 28.9-57.6% at 500-600 °C, and the acids were 0%-34.3%. Total selectivities of Aromatic and Aliphatic increased from 15.9% to 57.6%, with the increase in the weight ratio of catalyst to jatropha residues from 4 to 10, while the Acid selectivities decreased from 48.8% to 1.6%. As shown in Fig.2(d), with Ni2P/Beta(27), total Aromatic and Aliphatic selectivities were roughly 42.4-99.3% at 500-600 °C. Total selectivities of Aromatic and Aliphatic were 42.4%-96.5%, with the change in the weight ratio of catalyst to jatropha residues from 4 to 10. Thus, these four catalysts were effective for the pyrolysis reaction at very small-scale pyrolysis. In order to examine the effectiveness of catalysts at large-scale pyrolysis, fast pyrolysis was performed using stainless-steel reactor and both organic product selectivities and yields will be considered.

3.3 Fast pyrolysis of jatropha residue using stainless-steel reactor.

One aim of runs using stainless-steel reactors was to examine the effect of Cat/Jat ratio on the selectivities, where Cat/Jat = 0.35-0.76 is for the reactor, while Cat/Jat = 6.2 is for Py-GC/MS. Another aim is to estimate the yields of liquid products and then, to choose catalysts for regeneration tests. The jatropha residue was pyrolyzed using NiMo(O)/ZSM(38) in the stainless-steel reactor at 500-650 °C without and with catalyst. The products consist of gas (Gas), water-soluble liquid phase (Oil(water)), organic liquid phase (Oil(Organic)), char (Char), and unidentified (Unidentified). The two liquid phases were directly obtained from the iced and liquid nitrogen traps without any rinsed solvent and the organic phase, which appeared as black liquid, was subjected to GC-MS analysis, as mentioned later.

Temperature dependence of each yield is shown in Fig.3(a). The obtained bio-oil was separated upper and lower layer, the upper is organic liquid and the lower is water-soluble. The organic phase contained below 15 wt% water, as estimated by ultimate analysis. The organic phase yield decreased from 15.8% to 6.2% with the increase in the reaction temperature at 500-650 °C, while gas yield increased from 11.9% to 28.6%. Organic liquid products were analyzed by GC-MS. Relative selectivities are shown in Fig.3(b). The Aromatic included typically ethylbenzene, toluene, xylenes, indene and naphthalene. The Aliphatic included 1-decene, hexadecane and pentadecane. The total hydrocarbon selectivities increased from 42.6% to 60.1% with the increase in temperature at 500-600 °C and thereafter decreased to 56.8% at 650 °C. The phenols contained phenol, alkylphenol, 2-isopropoxyphenol and the phenol selectivities increased from 4.01% to 10.95% with the temperature increase. The acids contained typically hexadecanoic acid and octadecenoic acid and the acid selectivities decreased from 21.4% to 3.3% with the rising temperature. The N-compounds were typically benzylnitrile, indole, alkylindole, hexadecanenitrile and the selectivities were between 12.5% and 23.5%.

Catalyst dependence of each yield is shown in Fig.4. At 600 °C, the yield of organic liquid phase was between 8.7% and 11.7% (Fig.4(a)), while, at 500°C, the yield was 9.3%-24.5% (Fig.4(b)), being a little higher than that at 600 °C. The yields of gas, water phase and char at 600 °C was 7.5%-28.9%, 33.3%-44.0%, and 17.6%-31.8%, while, the yields at 500 °C were 9.2%-14.9%, 34.0%-38.6%, and 23.9%-

277 34.1%, respectively.

278 Relative selectivities in organic liquid products obtained by GC/MS are shown in **Tables S2-S4**. As
279 shown in **Table S2**, total selectivities of **Aromatic and Aliphatic** at 600 °C were in the order:
280 NiMo(O)/Y(14) (71.7%) > PtPd/ZSM(38) (68.8%) > Ni2P/Y(14) (65.4%) > NiMo(O)/Beta(27) (63.9%)
281 > NiMo(O)/ZSM(38) (60.1%) > Ni2P/Q(30) (53.7%) > NiMo(S)/Y(14) (53.4%) > Ni2P/ZSM(38)
282 (53.3%) > Ni2P/Beta(27) (47.2%) > Ni2P/ZrO₂ (40.4%) > None (36.4%). Acid selectivities were
283 PtPd/ZSM(38) (2.36%) < NiMo(O)/Y(14) (2.97%) < Ni2P/Q(30) (4.68%) < NiMo(O)/Beta(27) (5.41%)
284 < NiMo(O)/ZSM(38) (6.38%) < Ni2P/Y(14) (7.26%) < Ni2P/ZSM(38) (12.9%) < NiMo(S)/Y(14)
285 (19.1%) < Ni2P/Beta(27) (27.4%) < Ni2P/ZrO₂ (33.7%) < None (41.2%). At 500 °C, total selectivities
286 of **Aromatic and Aliphatic** were found to be a little lower than those at 600 °C, while Acid selectivities
287 increased with the decreased temperature. The **Aromatic and Aliphatic** selectivities at 500 °C were in
288 the order: PtPd/ZSM(38)(66.2%) > NiMo(O)/Y(14) (51.7%) > Ni2P/Y(14) (47.6%) >
289 NiMo(O)/ZSM(38) (42.6%) > NiMo(O)/Beta(27) (14.8%) > Ni2P/ZSM(38) (12.6%) > Ni2P/Beta(27)
290 (2.6%). When twice amount of jatropa residues (50g) was used with NiMo(O)/Y(14), Oil (organic)
291 yield was 21.3% and Oil(Water) yield was 28.6%, being total liquid yield of as much as 49.9%. As
292 shown in **Table S3**, in this case, the **Aromatic/Aliphatic** selectivities were 31.42% and Acid selectivities
293 were 52.98%. **Figure 5** shows a correlation between **Aromatic/Aliphatic** and Acids selectivities. The
294 NiMo(O)/Y(14), NiMo(O)/ZSM(38), NiMo(O)/Beta(27) and Ni2P/Y(14) are found to be favorable
295 catalysts. **From large-scale pyrolysis, Ni2P/Y(14) was found to be more effective than Ni2P/Beta(27).**
296 Thus, taking **Aromatic/Aliphatic** and Acid selectivities into account, Ni-based catalysts such as
297 NiMo(O)/Y(14) were found to be effective and comparable to PtPd/ZSM(38).

298 As shown in **Table S4**, the **Aromatic** included toluene, xylenes, methylindene, naphthalene, and
299 methyl naphthalenes, **which were formed by deoxygenation and dehydroaromatization of aliphatic**
300 **hydrocarbons and phenols [13]**. The **Aliphatic** included, typically, decene, pentadecane, hexadecene.
301 The Phenol included phenol, methylphenol and dimethylphenol. The Oxy products contained
302 benzenepropanal, benzofuran, and 2-methylbenzofuran. The acids and esters contained hexadecanoic
303 acid, octadecenoic acid (oleic acid), and octadecanoic acid (stearic acid). The N-comp. included
304 benzylnitrile, indole, methylindole, hexadecanenitrile. **Tables S2 and S3** exhibit the acid values of
305 organic liquid products. The values at 600 °C were 2.74-7.02 mg-KOH.kg⁻¹ for excellent four catalysts
306 such as **NiMo(O)/Y(14), NiMo(O)/ZSM(38), NiMo(O)/Beta(27) and Ni2P/Y(14)**, being much lower
307 than 28.2 mg-KOH.kg⁻¹ in the absence of catalyst. The acid value at 500°C was only 1.99 mg-KOH.kg⁻¹
308 for NiMo(O)/Y(14) catalyst, which was much lower than 38.7mg-KOH.kg⁻¹ of PtPd/ZSM(38).

309 **Figure S1** shows the effect of catalyst/jatropa (Cat/Jat) weight ratio on the yield and selectivities
310 using NiMo(O)/Y(14) at 600 °C. The yield of organic liquid phase decreased from 10.7% to 6.6% with
311 the increased ratio from 0.348 to 0.758, while the gas yield remained constant and water phase yield
312 decreased from 34.0% to 27.8% and char yield increased from 17.6% to 27.9%. The total hydrocarbon
313 selectivities increased from 71.7% to 83.0% with the increased ratio from 0.348 to 0.758 and the
314 phenols increased from 2.9% to 6.9%, whereas the Oxygenates and Acids selectivities decreased from
315 9.4% to 4.7% and from 3.0% to 1.2% with the raised ratio. Also, the N-compounds decreased from
316 12.3% to 3.7%. **These indicate that the hydrocarbon selectivities could increase through deoxygenation**
317 **and hydroaromatization with the increased Cat/Jat ratio and too much aromatization would lead to an**
318 **increase in char yield [13]**. Thus, the more catalyst, the less organic phase yield, but the more total
319 hydrocarbons, and the less acids, oxygenates and N-compounds resulted.

320 As shown in **Table 3**, the ultimate analysis of the organic liquid product exhibited 71-73% of carbon,
321 which was much higher than that of starting jatropa residue (46.4 %), while 14-17% of oxygen content
322 was lower than that of the starting residue (43 %). The estimated higher heating values (HHV) were 32-
323 33 MJ/kg, which was close to a HHV value of crude triglyceride [25]. Density of the bio-oil was 0.88-
324 0.89 g.cm⁻³, being comparable to diesel fuel (0.83-0.9 g.cm⁻³). Nitrogen content was 924-1220 µg.(ml)⁻¹
325 and sulfur content was 62-87 ppm. The acid values of 5.2-7.0 mg-KOH.kg⁻¹ was much lower than 28.2
326 mg-KOH.kg⁻¹ in the absence of catalyst. Thus, cheap Ni-based catalysts could be comparable to PtPd

catalysts and the obtained bio-oil has a desired carbon content and reduced acid value, although further up-grading will be required.

3.4 Effect of catalyst regeneration

The NiMo(O)/Y(14), NiMo(O)/ZSM(38) and Ni₂P/Y(14) catalysts were regenerated after use for pyrolysis as explained in the experimental section. The regenerated catalyst was used for pyrolysis of jatropha residues under the same conditions (at 600°C under N₂ flow at 1,900 ml/min in the stainless steel reactor). As shown in Fig.6A-1, by the first regeneration (Re1) and the second regeneration (Re2) of NiMo(O)/Y(14), the organic liquid product yield remained constant, but Gas and Water phase yields gradually decreased, but Char yield increased from 17.6% to 30.9%. Similar trends were observed for Ni₂P/Y(14) and Char yield increased from 25.3% to 34.1% (Fig.6A-3). For NiMo(O)/ZSM(38), both organic liquid product and Char yields remained constant after regeneration, but Gas and Water phase yields slightly decreased (Fig.6A-2). These indicate that catalyst regeneration would be more effective for ZSM(38) support than for Y(14) support, due to a difference of pore size [22]. As shown in Table 4, the surface area of NiMo(O)/Y(14) dramatically decreased after regeneration from 464 m².g⁻¹ to 255 m².g⁻¹, while only 10% decrease was observed for NiMo(O)/ZSM(38) from 223 m².g⁻¹ to 200 m².g⁻¹, being consistent with the results of char yield. **However, change in these physical structures would not have a critical impact on the catalyst performance.**

For NiMo(O)/Y(14), the order of total hydrocarbon selectivity was Re1(80.4%) $\cong$ Re2(80.1%) > Fresh(71.7%) and the phenols slightly increased from 2.9% to 5.3%, whereas the Oxygenates, Acids and N-compounds selectivities decreased from 9.4% to 5.0%, from 3.0% to 1.4% and from 12.3% to 7.8%, after regeneration, as shown in Fig.6B-1. For Ni₂P/Y(14), the order of total hydrocarbon selectivity was Re2(80.6%) $\cong$ Re2(79.3%) > Fresh(65.4%), whereas the other product selectivities slightly decreased: Phenols (6.1% $\rightarrow$ 2.9%), Oxygenates (11.7% $\rightarrow$ 7.1%), Acids (7.3% $\rightarrow$ 0.6%) and N-compounds (9.5% $\rightarrow$ 7.4%)(Fig.6B-3). For NiMo(O)/ZSM(38), the order of total hydrocarbon selectivity was Re1(64.6%) > Fresh (60.1%) and the phenols were constant and the Oxygenates and Acids selectivities decreased from 11.4% to 4.1% and from 6.4% to 1.7%, but the N-compounds increased from 12.5% to 20.7% (Fig.6B-2). Thus, these three Ni-based catalysts would have sufficient pyrolysis ability even after regeneration, comparative to PtPd/ZSM catalysts [23].

Conclusion

Cheap Ni-Based catalysts were explored for pyrolysis of jatropha residues to form bio-oil. First, a Py-GC/MS was used under the catalyst to jatropha ratio of 6.2 and four zeolite-based catalysts, NiMo(O)/ZSM(38), NiMo(O)/Y(14), NiMo(O)/Beta(27) and Ni₂P/Beta(27), were found to be promising candidates for total hydrocarbon formations. **But, in the large-scale pyrolysis, Ni₂P/Y(14) was found to be more effective than Ni₂P/Beta(27). In fact, when the pyrolysis was carried out using low catalyst/jatropha ratio of 0.35-0.76 and stainless-steel reactor, taking Aromatic/Aliphatic and Acid selectivities at both 600 °C and 500 °C into account, Ni-based catalysts such as NiMo(O)/Y(14), NiMo(O)/ZSM(38), NiMo(O)/Beta(27) and Ni₂P/Y(14) were found to be effective and comparable to PtPd/ZSM(38).** When jatropha residues (50g) was used with NiMo(O)/Y(14) at 500 °C, total liquid yield was as high as 49.9%, including 21.3% of organic liquid. The acid values of organic liquids obtained at 600 °C were 2.74-7.02 mg-KOH.kg⁻¹ for the above four catalysts, being much lower than 28.2 mg-KOH.kg⁻¹ in the absence of catalyst, while the acid value at 500°C was only 1.99 mg-KOH.kg⁻¹ for NiMo(O)/Y(14) catalyst, which was much lower than 38.7mg-KOH.kg⁻¹ of PtPd/ZSM(38). The estimated higher heating values (HHV) of the liquid were 32-33 MJ/kg. The NiMo(O)/Y(14), NiMo(O)/ZSM(38) and Ni₂P/Y(14) catalysts could be regenerated after use for pyrolysis and the organic liquid product yields remained constant and **total hydrocarbon selectivities were also constant within the experimental error.** Thus, under these pyrolysis conditions, Ni-based catalysts seems to be better and cheaper candidates than PtPd systems.

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462 Figure captions:

463 Figure 1: TPR profiles of the typical catalysts. **1:** NiMo(O)/Beta(27), **2:** NiMo(O)/Y(14),
464 **3:** NiMo(O)/ZSM(38)

465 Figure 2: Product selectivities for catalytic fast pyrolysis of jatropha residues. Reaction conditions:
466 catalyst to jatropha weight ratio:4-10, reaction temperature: 500 °C-600 °C. (a): NiMo(O)/ZSM(38), (b)
467 NiMo(O)/Beta(27), (c) NiMo(O)/Y(14), (d) Ni₂P/Beta(27). The number in the support denote Si/Al₂
468 ratio.

469 Figure 3: Temperature dependence of yields of oil/gas/char and selectivities of organic liquid product in
470 pyrolysis of jatropha residues using the stainless-steel reactor.

471 Conditions: Catalyst/Jatropha residues = 10/26 (=0.38), N₂ flow= 1900 ml/min. Gas:C1-C4
472 hydrocarbons +CO+CO₂, Oil(W): Water-soluble liquid, Oil(Org): Organic liquid, Char:
473 Carbon solid, Unidentified = 100 – (Gas+Oil(W)+Oil(Org)+Char).

474 Figure 4: Yields of oil, gas and char in pyrolysis of jatropha residues using Ni-based catalysts.

475 Conditions: See footnote of Figure 3. (a) 600 °C, (b) 500 °C.

476 Figure 5: Correlation between Aroma/Alkanes and Acids selectivities.

477 **1.** None, **2.** PtPd/ZSM(38), **3.** NiMo(O)/Y(14), **4.** NiMo(S)/Y(14), **5.** NiMo(O)/ZSM(38),
478 **6.** NiMo(O)/Beta(27), **7.** Ni₂P/ZSM(38), **8.** Ni₂P/Y(14), **9.** Ni₂P/Beta(27), **10.** Ni₂P/ZrO₂, **11.** Ni₂P/Q30

479 Figure 6: Effect of catalyst regeneration. **A:**Yield, **B:** Product Selectivities of Oil(Org). A-1 and B-1:
480 NiMo(O)/Y(14), A-2 and B-2: NiMo(O)/ZSM(38), A-3 and B-3: Ni₂P/Y(14). Conditions: See
481 footnote of Figure 3.

482 Figure S1: Effect of Catalyst/Jatropha weight ratio at 600 °C. **(a)** Yields, **(b)** Selectivities of Oil(Org).
483 Conditions: See footnote of Figure 3.

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Table 1 Proximate and Ultimate Analyses of Jatropha Residue.

Proximate analysis (%)	
moisture	4.95
volatile matter	81.0
ash content	0.76
fixed carbon	11.39
Ultimate analysis (%)	
C	46.39
H	6.55
N	4.53
O	42.53

Table 2. Catalyst Properties

Catalyst ^a	Particle size/nm ^b		Physical properties		
	Ni	Mo	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
ZSM(38)	-	-	353.0	0.227	2.58
Pd Pt/ZSM(38)	0.151(Pt)	0.275(Pd)	266.4	0.250	3.76
NiMo(O)/ZSM(38)	14.3	28.0	222.8	0.218	3.19
NiMo(O)/Beta(27)	25.1	62.2	176.0	0.247	5.62
NiMo(O)/Y(14)	8.42	20.9	464.5	0.174	1.50
NiMo(S)/Y(14)	21.3	52.9	341.7	0.098	11.5
Ni2P/ZSM(38)	39.8	-	194.4	0.171	3.53
Ni2P/Y(14)	36.5	-	323.6	0.286	3.53
Mi2P/Beta(27)	49.0	-	165.1	0.238	4.12
Ni2P/ZrO2	11.6	-	35.1	0.134	15.2
Ni2P/SiO2(Q30)	33.0	-	63.7	0.182	11.4

^a Ni: 10 wt%, Mo:30 wt%. Pt:0.5 wt%, Pd:0.5 wt%. The numbers in parentheses denote Si/Al₂ ratio.

^b The sizes are estimated by CO adsorption.

Table 3 Properties of pyrolysis bio-oil (organic phase) from jatropha residues.

	Pyrolysis Bio-oil at 600°C			
	No Catalyst	NiMo(O)/Y(14)	NiMo(O)/ZSM(38)	Ni2P/Y(14)
Yield of bio-oil (organic phase)/% ^a	9.11	10.7	9.45	9.92
Ultimate analysis ^b				
C	67.20	72.99	71.61	70.83
H	8.79	7.84	7.52	7.61
N	5.57	4.97	5.61	5.01
O	17.33	13.86	15.26	16.47
HHV/ MJ/kg ^c	32.16	33.38	32.21	31.85
Density/g/cm ³	0.854	0.890	0.877	0.890
N/ mg/ml	-	1020	1220	923.9
S/ ppm	-	87.15	62.48	82.59
Acid value/mg-KOH/kg	28.20	5.88	5.24	7.02

^aYield = (weight of organic liquid)/(jatropha residues initially introduced) x100. ^bThe ultimate analysis was carried out using organic phase product. ^cEstimated by Dulong's equation.

Table 4. Effect of regeneration on the catalyst properties^a

Catalyst	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)
NiMo(O)/Y(14)-Fresh	464.5	0.174	1.50
NiMo(O)/Y(14)-Re1	345.4	0.203	2.50
NiMo(O)/Y(14)-Re2	255.0	0.229	3.59
NiMo(O)/ZSM(38)-Fresh	222.8	0.218	3.19
NiMo(O)/ZSM(38)-Re1	191.9	0.194	3.88
Ni2P/Y(14)-Fresh	323.6	0.286	3.53
Ni2P/Y(14)-Re1	300.5	0.277	3.54
Ni2P/Y(14)-Re2	296.8	0.265	3.57

^a Reaction temp.:600°C. “Fresh” denotes the pyrolysis reaction was carried out using fresh catalyst. “Re2” denotes the reaction using the used catalyst after the second regeneration at 600°C.

Fig.1

TPR

Fig.2 NiMoO-Z38

NiMoO-B27

NiMoO-Y14

Ni2P-B27

Fig.3

Fig.4

Fig.5