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Effect of Metal-modified Carbon Catalysts on Fast Pyrolysis of Jatropha Waste

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Screening, synthesis, and testing of metal-modified carbon catalysts for fast pyrolysis of Jatropha waste were carried out using Pyro-GCMS (Py-GC/MS) and a quartz reactor. Our results suggest that activated carbon-based catalysts, especially those impregnated with Ni, are effective catalysts. The selectivity for aromatic and aliphatic hydrocarbons was 79.4 %, with relatively low amounts of oxygenated compounds or other unfavorable components. Using Ni/C catalyst in a quartz reactor, the selectivity for aromatic and aliphatic hydrocarbons was 64.1 %. Successive reaction through hydrogen migration over the metal-modified activated carbon catalyst surface could occur at 600 ℃. Further improvements of catalyst activity and the reactor configuration may be required to produce liquid fuel commercially.

Keywords

Fast pyrolysis, Jatropha waste, Activated carbon catalyst, Nickel-activated catalyst, Aromatic hydrocarbon, Pyrolysis GCMS

1. Introduction

Biofuels[1)] are becoming an important potential replacement for fossil fuels, but are controversial, particularly with respect to the consequent disruption of the food chain. Recent spikes in commodity and grains prices are believed to be directly linked to the use of these staple foods as biofuel feedstock. In principle, the raw material for biofuel production should come from non-edible sources. Jatropha, a non-edible plant that readily grows in many regions and climates, is one such feedstock. Oil can be extracted from Jatropha seeds, with Jatropha waste as byproduct. Several methods can be employed to collect additional oils *via* pyrolysis of this Jatropha waste.

The *Jatropha curcas* L. (JCL) plant is currently receiving a great deal of attention[2)~4)], because of its distinct advantages over other tropical oil-producing trees and plants. In particular, JCL is drought-resistant and may grow in extreme conditions[2)]. The oil is toxic, and JCL planting does not compete directly with food production, which is of prime importance for non-food biomass. The fruit is rich in carbohydrates[2)] so could be used for bio-ethanol production by fermentation[5)]. Jatropha waste, the residue after oil extraction, may be used, after detoxification, as animal feed[2)]. The fibers may be applied as a binder in construction materials, and various parts of the trees contain interesting components with potential pharmaceutical uses. The shell of the seeds is rich in lignin and may be used for energy generation[3)]. Without such efficient utilization of JCL waste byproducts, large amounts of waste products will be produced at the processing units, with negative impacts on the environment. Thus, to make the JCL business viable, JCL waste must be converted into liquid products.

Fast pyrolysis involves rapid heating of raw materials to relatively low temperatures of 300-600 ℃[6)] resulting in the formation of mainly liquid products. However, these liquid products may consist of hundreds of compounds, ranging from aliphatic, aromatic, polyaromatic, and phenolic to various oxygenated hydrocarbons and acids[7)]. Therefore, the liquid products of fast pyrolysis cannot be used directly, and require costly upgrading processes that undermine the overall economic benefits. Consequently, *in-situ* upgrading of liquid products from pyrolysis must be prioritized, to minimize the quantity of oxygen-containing compounds. We recently reported catalytic fast pyrolysis in the presence of unmodified zeolite catalysts by which aromatic and aliphatic hydrocarbons were favorably produced using the Py-GC/MS

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technique[8] on very small scales.

Generally, metal-modified carbon catalysts are effective for dehydrogenation of paraffins and alcohols into olefins and aromatic hydrocarbons[9]. Hydrogen migration (spill-over) effects are important in the dehydrogenation reaction over these catalysts[10]. These carbon catalysts have been used for hydrodeoxygenation (HDO) of phenol derivatives using Pd/C[11] and for HDO of pyrolysis oil using Ru/C[12]. However, HDO using Pd/C and Ru/C is performed under high pressure hydrogen conditions, whereas catalytic fast pyrolysis is usually carried out under no hydrogen conditions[8]. Zeolite catalysts are effective for catalytic fast pyrolysis of woody biomass[13] and Jatropha[14], even under no hydrogen conditions. However, the use of metal-modified carbon catalysts for the catalytic pyrolysis of any biomass at atmospheric pressure conditions has not been described. Therefore, we decided to experiment with metal-modified carbon catalysts for pyrolyzing Jatropha waste and *in-situ* upgrading under atmospheric pressure conditions.

The present study examined dehydrogenation and HDO over metal-modified carbon catalysts under the conditions of fast pyrolysis of Jatropha waste using the Py-GC/MS technique. The results using the quartz reactor were compared with those of Py-GC/MS.

2. Experimental

2. 1. Materials

Jatropha waste was obtained from a Thailand company. The waste was compressed into tablet shapes, followed by dividing and sieving into particles of 2-3 mm diameter before pyrolysis. To explore novel potential catalysts with activity for deoxygenation as well as denitrogenation, the commercially available carbon catalysts 5 %-Pd/C, 5 %-Ru/C, 5 %-Pt/C and 5 %-Rh/C were tested as controls (N. E. Chemcat Corp.). Activated carbon (Aldrich, Darco G-60, 100 mesh) and Jatropha waste were also individually tested for comparison. The amount of metal-modified catalysts used was set at 2.5 mg, and the weight of Jatropha residue was set at 0.4 mg, which was used without any pretreatment. Other catalyst candidates were prepared as follows: 5 %-Co/C, 5 %-Fe/C, 5 %-Mo/C, and 5 %-Ni/C, in which C denotes activated carbon. Chemicals used for catalyst preparation were as follows. $Fe(NO_3)_3 \cdot 9H_2O$ (Wako); $Ni(NO_3)_2 \cdot 6H_2O$ (Wako); $Co(NO_3)_2 \cdot 6H_2O$ (Wako); and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Kokusan Chemical Works, Ltd.). The catalysts used in this study were prepared by impregnating the required catalyst supports with the metal sources, followed by drying at 100 ℃, and calcination for 5 h at 300 ℃ for the carbon support. All catalysts were pre-reduced for 5 h at 250 ℃ under 4 MPa of H_2 prior to the pyrolysis reaction.

2. 2. Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained on a Philips 1850 diffractometer in step mode employing CuKα radiation ($k = 0.154$ nm). The X-ray tube was operated at 40 kV and at 40 mA. The average metal and metal oxide particle sizes (d) were calculated using the Scherrer formula,

$$d = 0.90\lambda/(\beta\cos\theta) \quad (1)$$

where λ is the wavelength of the X-rays (0.154 nm), β is the width in radians at the half height of the diffraction peak, and θ is the glancing angle.

The reducibility of the prepared catalysts such as Ni/C and Mo/C was studied by H_2-temperature-programmed reduction (TPR). Before the analysis, 50 mg of the sample was placed in a quartz tube and purged with Ar at 200 ℃ for 1 h to remove any impurities from the catalyst surface. The sample was then cooled to room temperature in flowing He. TPR measurement was then carried out using a 3 % H_2/Ar (v/v) mixture (flow rate: 30 mL/min) at a heating rate of 5 ℃/min from room temperature to 800 ℃. The H_2 consumption was recorded using a thermal conductivity detector (TCD). The BET surface area and BJH pore size distribution of all the catalysts were determined by N_2-physisorption using a Belsorp-max apparatus (Bel Japan, Inc.) at liquid N_2 temperature −196 ℃).

2. 3. Proximate and Ultimate Analyses of Jatropha Waste

Proximate analysis of Jatropha waste was performed in nitrogen using a thermogravimetric analyzer (TGA) (TG 2000, Bruker AXS)[15]. The sample (approximately 10 mg) was heated from 40 to 800 ℃ at a typical ramp rate of 100 ℃/min in a total Ar flow rate of 50 mL/min. The moisture content was considered to account for the weight loss as the sample was heated up to 160 ℃. Two-step devolatilization was assumed to begin at 160 ℃ and was completed at 600 ℃. TGA pyrolysis showed a gradual loss in mass above 600 ℃, which can be attributed to volatile metal loss and carbonate decomposition. TGA analyses in the presence of catalyst were performed using measurement conditions of sample 5 mg, catalyst 5 mg, Ar flow rate 30 mL/min, temperature range 30-800 ℃ and heating rate 20 ℃/min. The ultimate analysis was performed using a CE Instruments EA1110 analyzer. The results of proximate and ultimate analyses are given in **Table 1** with data from the literature[16].

2. 4. Pyrolysis and Analysis

2. 4. 1. Pyro-GCMS (Py-GC/MS) Analysis and GC/MS Analysis

Py-GC/MS is useful for fast pyrolysis of solid sample at 550 ℃, whereas GC/MS analysis is performed at 320 ℃ using liquid bio-oil sample. The analysis was performed with a PY-2020iS pyrolyzer (Frontier Labs) connected to an Agilent Model 7890A gas chromato-

Table 1 Proximate and Ultimate Analyses of Jatropha Waste

Proximate analysis	[%]	
moisture		8.05
volatile matter		84.8
ash content		4.44
fixed carbon		2.71
Ultimate analysis	[%]	
C		49.25
H		6.10
N		3.38
O		41.27

graph (GC) interfaced with an Agilent model 5975C mass spectrometer (MS). Jatropha waste was sieved prior to use. Samples (0.4 mg) in the holder were rapidly pyrolyzed at 550 ℃ by dropping the sample holder into the furnace. If a catalyst was used, the weight ratio of waste/catalyst sample was 0.16: 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 70 ℃ for 1 min, ramp to 400 ℃ at 20 ℃/min, and hold at 400 ℃ for 15 min. Product selectivities were evaluated by area% of each peak detectable by the GC/MS.

2. 4. 2. Catalytic Fast Pyrolysis Experiment Using a Quartz Reactor

As shown in **Fig. 1(A)**, pyrolysis experiments were carried out using a quartz reactor with a diameter of 4.4 cm and total height of 50 cm, with two types of trap (ice and liquid N_2), and a gas reservoir in the form of a plastic bag. The reactor was connected with an electronic mass flow controller to regulate the flow rate of nitrogen into the reactor. The reactor was heated by an electric furnace, in which the reaction temperature was measured at the catalyst bed. A quartz frit disc was installed 10 cm above the reactor bottom to retain approximately 5 g of catalyst in place. The feeding of the raw material was done semi-continuously through 1-cm diameter tubing at the top of the reactor. The waste was first pelletized into a coin-like chip using a manual hydraulic pelletizer, then divided into small 2-3 mm pieces for feeding into the reactor. The total of raw material fed was around 10 g over a runtime of 30 min. Carrier gas was introduced from the top of the reactor and flushed the product gas through the bottom of the reactor. Standard conditions were as follows: Waste/Catalyst 2, Temperature 600 ℃, N_2 flow 425 mL/min, Residence time in reactor base 1.48 min[6]. For QR-800-NiC catalyst, N_2 was 800 mL/min and the residence time was 0.79 min.

$$\text{Residence time} = \text{Reactor volume}\,(632\ \text{mL})/N_2\ \text{flow rate}\,(\text{mL/min}) \quad (2)$$

Product gas from the reactor was then passed through a series of ice-cooled and liquid nitrogen-cooled condensers for collection of the liquid product before entering a gas bag for further analysis. After the reaction, all gaseous and liquid products were collected and analyzed by off-line hydrogen-flame ionization detector (FID) and TCD gas chromatography. Porapak Q and MS 5A columns for TCD were used for gaseous products. FID analysis of gaseous hydrocarbon products was performed using a KCl-PLOT column. Liquid products were extracted in 10 mL of acetone and all liquid phases were analyzed using two FID-GCs, in which UA-DX30 and UA-CW columns were used. For FID analysis, dioxane was used as the internal standard. Also, GC/MS analysis of the liquid sample used injection temperature of 320 ℃. Product selectivity was defined as moles of carbon in each product divided by the total carbon in the feed. The amount of carbon deposited over the catalyst surface was analyzed in air by thermogravimetric (TG) analysis, where the amount of deposited carbon was approximately estimated by TG weight loss between 150 ℃ and 400 ℃, and the carbon support was combusted above 400 ℃, as discriminated by the differential thermogravimetry analysis (DTG) profiles.

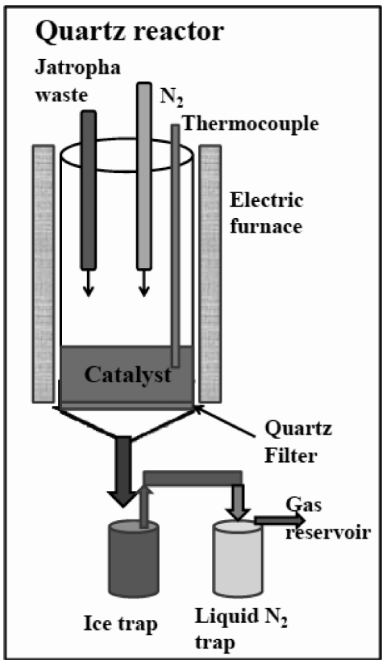


Fig. 1 Quartz Reactor for Pyrolysis

3. Results and Discussion

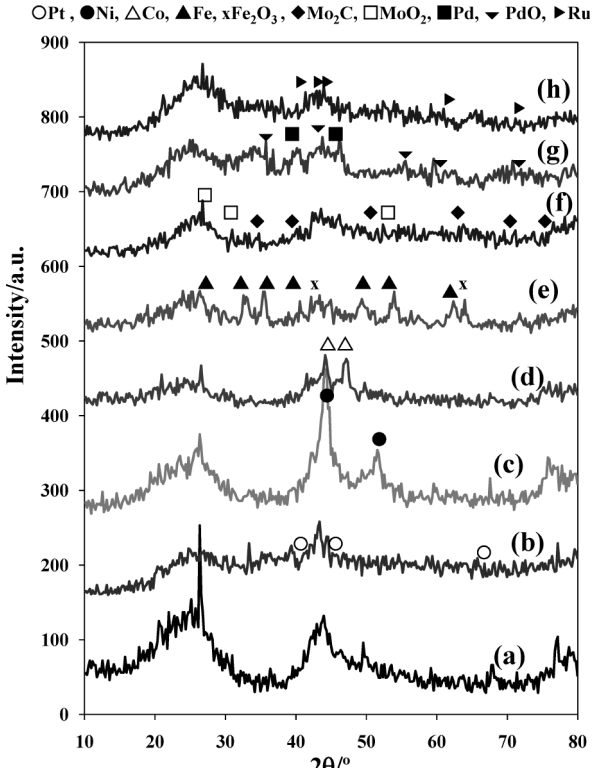
3. 1. Catalyst Properties

XRD patterns of the activated carbon-based catalysts, synthesized with different metal sources such as Ni, Co, Fe and Mo, followed by H_2 reduction at for 5 h at 250 ℃ under 4 MPa, are presented in **Fig. 2**. For the Ni and Co/activated carbon (C) catalysts (**Fig. 2** (c),

(d)), mean Ni and Co metal particle sizes of 5.754 nm and 9.296 nm were determined using the Scherrer formula with the Ni [111] diffraction peak at $2\theta = 44.37°$ and Co [100] at 47.30°. For the Fe/C catalyst (**Fig. 2** (e)), Fe metal and Fe_2O_3 were detected. The Fe metal particle size was 11.19 nm with the [110] peak at $2\theta = 35.56°$, whereas the Fe_2O_3 size was 20.1 nm with the [110] peak at $2\theta = 63.17°$. For the Mo/C catalyst (**Fig. 2** (f)), no metallic Mo was detected at $2\theta = 40.6°$ and 73.99°, but Mo_2C (21.12 nm) was formed with the [101] peak at $2\theta = 39.8°$ and MoO_2 (10.59 nm) was detected with the peak at 26.73°. For commercially available Pd/C (**Fig. 2** (g)), the mean Pd metal particle size was 17.52 nm, whereas the size of Pt/C (**Fig. 2** (b)) was 10.20 nm. All XRD data are summarized in **Table 2**.

Surface properties, like BET surface area, pore volume, and average pore diameter of the catalysts are also summarized in **Table 2**. Surface area, pore volume, and average pore diameter of the activated carbon-based catalysts were 890-1370 m^2/g, 0.717-0.916 cm^3/g, and 2.64-3.73 nm, respectively. The average pore diameter of these catalysts was generally smaller than the metal particle sizes, indicating that almost all metal was located on the outer surface of the activated carbon. However, metallic Ni had a particle size (5.754 nm) close to the pore diameter of 3.73 nm, indicating high metal dispersion.

Figure 3 shows the characteristic reduction behavior of the carbon-based catalysts measured in TPR experi-



(a) AC, (b) 5 %-Pt/C, (c) 5 %-Ni/C, (d) 5 %-Co/C, (e) 5 %-Fe/C, (f) 5 %-Mo/C, (g) 5 %-Pd/C, (h) 5 %-Ru/C.

Fig. 2 X-ray Diffractograms of Carbon-based Catalysts after Pre-reduction

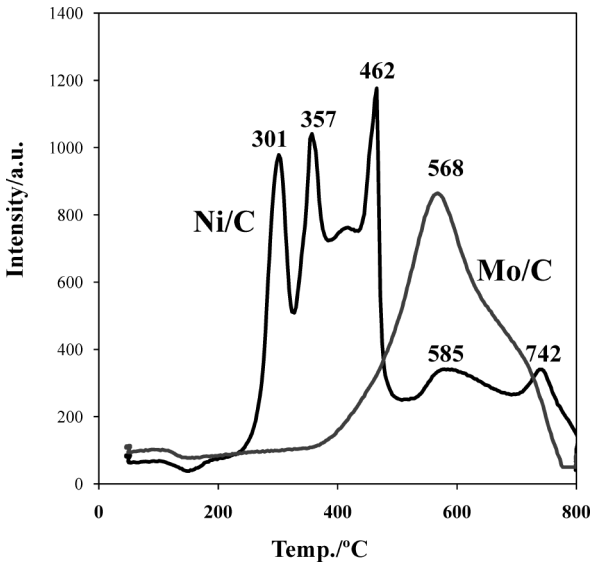


Fig. 3 TPR Profiles of Typical Catalysts

Table 2 Catalyst Properties

Catalyst	XRD crystallite size [nm]		Physical properties		
	Metal [nm]/[hkl] Carbide [nm]/[hkl]	Oxide [nm]/[hkl]	S_{BET} [$m^2\ g^{-1}$]	Pore volume [$cm^3\ g^{-1}$]	Pore diameter [nm]
AC[a)]	-	-	1026.3	0.916	3.57
5 %-Pd/C	17.52/Pd[200]	16.68/PdO[200]	1027.6	0.68	2.6475
5 %-Rh/C	-	-	-	-	-
5 %-Ru/C	27.81/Ru[101]	-	1371.4	0.905	2.64
5 %-Pt/C	10.20/Pt[111]	-	1127.1	0.805	2.86
5 %-Ni/C	5.754/Ni[111]	-	769.5	0.717	3.73
5 %-Mo/C	21.12/Mo_2C[101]	10.59/MoO_2[b)]	895.09	0.773	3.45
5 %-Fe/C	11.19/Fe[110]	20.10/Fe_2O_3[110]	937.13	0.802	3.42
5 %-Co/C	9.296/Co[100]	-	992.7	0.871	3.51

a) AC denotes activated carbon. b) No [hkl] data.

ments. For the Ni/C catalyst, three sharp peaks at 301, 357, and 462 ℃ were attributed to the reduction of well-dispersed Ni-containing phases, and the two broad peaks at 585 ℃ and 742 ℃ indicated the reduction of Ni^{2+} in strong interaction with the activated carbon support[17]. TPR analysis of the Mo/C catalyst showed that the reduction of molybdenum oxides began at above 400 ℃ and that the peak temperature was 568 ℃. However, a different reduction shoulder peak is evident at higher temperatures, above 600 ℃, where several MoOx suboxides can be formed. These results show that the reducibility of supported molybdenum oxides can be altered by the degree of Mo-support chemical interaction, and the nature of the surface species developed during preparation of the Mo/C samples[18]. Investigation of these TPR and XRD data demonstrates that the reduction of Ni in the Ni/C catalyst began at 231 ℃ and the first peak was observed at 301 ℃, indicating that, under the hydrogen reduction conditions at 250 ℃, metallic Ni was formed, but metallic Mo could not be detected, although MoC could be formed.

3. 2. Effect of Various Catalysts Using Py-GC/MS

The catalytic fast pyrolysis of Jatropha waste was carried out with different catalysts. **Table 3** shows the product selectivity as estimated by Py-GC/MS analysis, 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 CH_4, CO, and CO_2. All catalysts were reduced with hydrogen at 250 ℃ prior to use, whereas commercially available catalysts such as Pd/C, Ru/C, Pt/C, and Rh/C were used without reduction. The distribution of compounds in bio-oils was determined using a semiquantitative 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 (Aromatic), phenols (Phenol), alcohols and ketones (Alc-ketone), ethers (Ether), acids and esters (Acid-ester), alkanes and alkenes (Alkane-alkene), nitrogen-containing hetero compounds (N-hetero), nitrogen-containing noncyclic compounds (N-nonhetero) and others (Others). The aromatic hydrocarbons included monoaromatics and polyaromatic hydrocarbons (PAHs)[19], such as benzene, toluene, xylenes, methylindene, and methylnaphthalene. The typical phenolic compounds were phenols, alkylphenols, methoxyphenols and naphthalenols. The alcohols and ketones included 1H-indene-1-one, 1-methylcyclopropane methanol, 2-ethyl cyclohexanol, and 3-methyl-1,2-cyclopentadienone. Typical ethers included butenylmethyl ether and 2-methyl furan. The acids and esters contained acetic acid, hexadecanoic acid (palmitic acid), octadec-9-enoic acid (oleic acid), and octadecanoic acid (stearic acid)[20]. The aliphatic hydrocarbons (alkanes and alkenes) included cyclododecene, 5-octadecene and pentadecane and heptadecane. (N-hetero) compounds contained pyridine and quinoline and indole derivatives, and (N-nonhetero) compounds included nitrile and amide derivatives such as benzyl nitrile and hexadecanenitrile. (Others) contained Si-containing compounds such as decamethyltetrasiloxane.

In the absence of a catalyst, fast pyrolysis of Jatropha waste resulted in the major fraction (62.3 %) consisting of (Acid-ester). (Phenol) accounted for 17.2 %, and (Alc-ketone), (Ether) and (Aromatic) and (Alkane-alkene) were also found in lesser quantities. (N-hetero) and (N-nonhetero) were present in smaller amounts of 5.28 % and 1.01 %, respectively. Addition of activated carbon (AC) significantly changed the product distribution, as seen in **Table 3**. The proportion of (Aromatic) compounds (63.0 %) increased, whereas (Acid ester) and (Phenol) compounds were greatly reduced, and (N-hetero) and (N-nonhetero) were somewhat increased, indicating that more improvement of catalyst activity is still required to produce bio-oil

Table 3 Relative Proportions (area%) of Non-catalytic and Catalytic Fast Pyrolysis of Jatropha Waste Using Py-GC/MS[a)]

Catalyst	Area%[b)]								
	Aromatic	Phenol	Alc-ketone	Ether	Acid-ester	Alkane-alkene	N-hetero	N-nonhetero	Others
Non	1.06	17.2	3.92	6.4	62.3	2.46	5.28	1.01	0.4
AC[c)]	63.0	9.49	2.16	3.1	4.56	2.45	8.63	5.65	0.94
Pd/C	68.2	3.61	0	0	0	17.4	4.01	4.72	2.11
Rh/C	68.1	7.98	0	0	11.2	0	0	6.99	5.79
Ru/C	58.3	8.58	0	0.75	6.48	4.51	6.67	12.4	2.32
Pt/C	40.7	2.11	0	0	23.5	29.5	1.04	3.09	0
5 %-Ni/C	73.9	5.82	0.8	0	1.86	5.57	7.03	5.01	0
5 %-Mo/C	71.9	1.78	0	6.65	0	7.74	2.92	8.26	0.77
5 %-Fe/C	41.4	12.5	8.86	10.6	18.9	0	0	0	7.88
5 %-Co/C	43.9	26.2	9.8	3.3	5.71	5.14	2.44	3.51	0

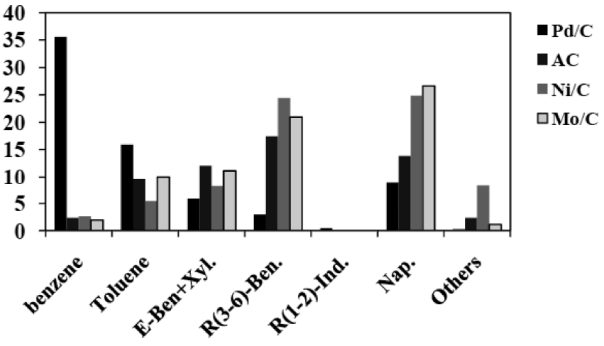
a) Reaction conditions: catalyst to sample weight ratio 6.25, reaction temperature 550 ℃. b) Product classifications: See p. 376-377 of text. c) AC denotes activated carbon.

with acceptable quality from Jatropha waste.

Addition of metal-modified carbon catalysts improved hydrocarbon yields to different extents depending on the catalyst. Pd/C enhanced (Aromatic) and (Alkane-alkene) production, whereas no (Alc-ketone), (Ether), or (Acid-ester) components except (Phenol) compounds remained. For Ru/C and Rh/C catalysts, 6.48 % and 11.2 % of (Acid-ester) still remained, indicating that deoxygenation was not complete. (Phenol) compound yields using these two catalysts were quite similar, but much higher proportions of (N-hetero) and (N-nonhetero) products were found with Ru/C than with non-catalytic pyrolysis. Pt/C catalyst had moderate efficiency for deoxygenating reactions, in which relatively large amounts of (Acid-ester) remained.

Table 2 shows that metal particle sizes in Ni/C and Co/C were 5.754 nm and 9.296 nm, whereas the metal particle size of Fe/C was 11.19 nm and that of Mo_2C was 21.12 nm. As seen in **Table 3**, both Mo/C and Ni/C catalysts showed good selectivity for (Aromatic) formation, with 71.9 % and 73.9 % yields, respectively. (Alc-ketone), (Ether) and (Acid-ester) compounds yields were not high, and total (N-hetero) and (N-nonhetero) compounds were 11-12 % for both catalysts. Selectivity for (Aromatic) hydrocarbons was 41 % and 44 % for Co/C and Fe/C, respectively, a little lower than those of Ni/C and Mo/C catalysts. In contrast, the sum of selectivity for oxygenates such as (Alc-ketone), (Ether), and (Acid-ester) was 45.01 % for Co/C and 50.86 % for Fe/C, higher than 19.31 % for activated carbon and 8.48 % for Ni/C. These findings demonstrate that the use of Co/C or Fe/C could make oxygenates formation more favorable than Ni/C and activated carbon. The Co/C and Fe/C catalysts, therefore, do not seem to be good candidates.

The aromatic distribution from catalytic fast pyrolysis of Jatropha waste is shown in **Fig. 4**, where catalysts such as non-metal-modified activated carbon, metal-modified (Pd/C), and base metal-modified (Ni/C and Mo/C) showed good aromatic product distributions. For Ni/C and Mo/C, the selectivities for naphthalenes and R3-6 substituted benzenes were above 20 % and other aromatic selectivities decreased as xylenes + ethylbenzene > toluene > polyaromatics (Others) ≅ benzene. The R3-6 substituted benzenes contained trimethyl benzenes and hexamethyl benzenes, and the polyaromatics contained anthracene and pyrene. The selectivities of activated carbon for naphthalenes, R3-6 substituted benzenes, xylenes + ethylbenzene, and toluene were between 10 % and 18 %. Pd/C showed high selectivities for benzene and toluene, whereas the selectivities for R3-6 substituted benzenes and polyaromatics were low. Carbon-based non-acidic cheap catalysts such as Ni/AC were very effective for improving aromatic selectivity. In the next section, the liquid yield from pyrolysis of Jatropha waste will be briefly examined based on thermogravimetric analysis (TGA).

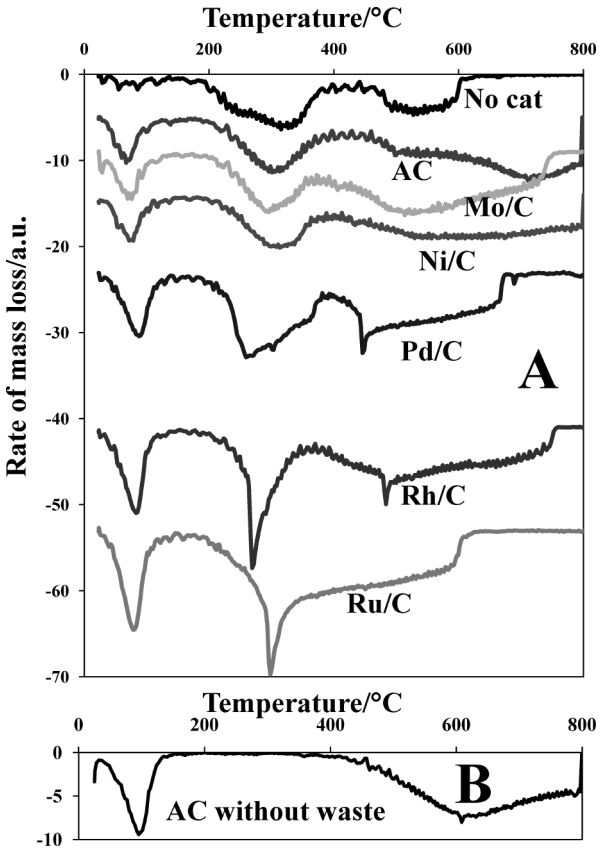


Reaction conditions: See Table 3. Aromatics measured include *benzene*, *Toluene*, *E-Ben.* + *Xyl.*: ethyl-benzene, xylenes, *R(3-6)-Ben.*: tri- or hexa-alkyl-benzene, *R(1,2)-Ind.*: indane or indene derivatives, *Nap.*: naphthalene or alkylnaphthalenes, *Others*: PAH such as phenanthrene.

Fig. 4 Aromatic Selectivity for Catalytic Fast Pyrolysis of Jatropha Waste

3. 3. Thermogravimetric Analysis of Jatropha Waste in the Presence of Catalysts

Relative product selectivities can be estimated by Py-GC/MS runs, but this does not provide adequate data for liquid yield. Therefore, TG and DTG analysis was carried out to roughly estimate the weight loss during pyrolysis in the presence of catalyst associated with liquid yield. As shown in the DTG data (**Fig. 5A**), waste without catalyst (No cat.) undergoes a stepwise degradation pathway that corresponds to the thermal decomposition of the different waste components. After removal of moisture, the first weight loss is followed by the second carbonization, volatile metal loss, and carbonate decomposition[15]. The first devolatilization step (200-400 ℃) can be attributed to the decomposition of carbohydrate components such as hemicellulose and cellulose, and the second step at 450-600 ℃ could, at least in part, represent the degradation of lipids from Jatropha oil, as well as lignin[15]. In this case, the weight losses in the first and second devolatilizations were 2.48 mg (49.6 %) and 1.76 mg (35.2 %), so total volatile matter was estimated to be 4.24 mg (84.8 %), as shown in the proximate analysis in **Table 1**. The decomposition of the mixture of waste and activated carbon catalyst undergoes a somewhat complex process due to the concomitant degradation of the activated carbon. The peak attributed to the removal of moisture became larger after addition of activated carbon, which could be due to moisture in the catalyst, as shown by the DTG of activated carbon without the waste (**Fig. 5B**). In fact, the moisture removal step and the first devolatilization step from 200-400 ℃ are similar to those with the no-catalyst sample. However, the second devolatilization at 450-600 ℃ could be accompanied by the degradation of activated carbon[21].



A: with Jatropha waste, B: only activated carbon without Jatropha waste.

Fig. 5 DTG Profiles Recorded for Active Carbon-based Catalysts in an Argon Atmosphere

Table 4 Devolatilization Parameters Obtained from TG and DTG[a)]

Catalyst	IT [℃][c)]	PT [℃][d)]	Weight loss [mg (%)]
No-cat[a)]	137.2	312.2	2.48 (49.6)
AC[b)]	162.3	297.8	2.21 (44.2)
5 %-Pd/C	139.1	270.4	3.39 (67.8)
5 %-Rh/C	160.5	279.5	2.59 (51.8)
5 %-Ru/C	167.0	308.2	2.86 (57.2)
5 %-Ni/C	158.8	307.0	2.37 (47.4)
5 %-Mo/C	158.8	299.8	2.35 (47.0)

a) Jatropha waste (5 mg) was used for TG. b) AC denotes activated carbon. c) Initial temperature of the second volatile loss (IT) after water evaporation. d) Peak temperature at maximum rate of weight loss (PT).

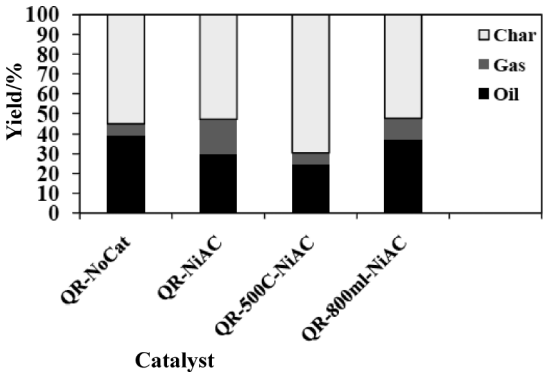


Fig. 6 Pylolysis of Jatropha Waste Using Quartz Reactor

Consequently, the second-step weight loss is very difficult to estimate for the mixtures of the waste sample and activated carbon-based catalysts such as Mo/C, Ni/C, Pd/C, Rh/C, and Ru/C. **Table 4** summarizes the first devolatilization step, in which initial (IT) and peak (PT) temperatures, and weight loss are estimated. The IT value is the initiation temperature of the second weight loss, which is estimated by the highest DTG value, whereas the PT value is estimated by the lowest DTG value. The peak temperatures were 270-340 ℃ and the weight losses were 44-68 %. These DTG findings indicate that all pyrolysis reactions to form liquid product could occur below 600 ℃, and that Py-GC/MS measurements at 550 ℃ might be optimum. In the next section, fast pyrolysis in the quartz reactor at 600 ℃ is examined using Ni/C, which showed good aromatic product distributions.

3. 4. Fast Pyrolysis Using a Quartz Reactor

The object of runs using reactors was to estimate carbon mass balance and to compare product selectivity with the Py-GC/MS results. In the quartz reactor, N_2 flow was 425 mL/min and residence time was 1.48 min, representing moderate pyrolysis conditions[22)]. As shown in **Fig. 6**, the yield of (oil + gas) was summarized as follows: Ni/C catalyst > no catalyst, reaction temperature of 600 ℃ > 500 ℃, and residence time of 1.48 min (N_2 = 425 mL/min) ≅ 0.79 min (N_2 = 800 mL/min).

Table 5 and **Fig. 7** summarize the GC/MS data of pyrolysis oil from Jatropha waste with and without catalyst. The pyrolysis oil is a combined liquid obtained from the ice trap and the liquid N_2 trap. Detectable products include aromatic hydrocarbons, phenols, alcohols/ketones, ethers, acids/esters, alkane/alkenes, N-heterocycle compounds, and N-nonheterocycle compounds. The products are similar to those obtained during runs using Py-GC/MS of solid waste sample, but the product distributions are slightly different. In fact, the relative selectivity for aromatics such as alkylbenzene, naphthalene, methylnaphthalene, and fluorene was estimated as 39.9 % for Ni/C (QR-Ni/AC), lower than 73.9 % for Py-GC/MS data (5Ni/AC in **Fig. 7**). The total percentage of phenols was calculated as 9.1 % (5.82 %) (Following numbers in parentheses denote the selectivities for the Py-GC/MS run). The total percentage of alcohols and ketones was 2.41 % (0.8 %). In this case, ethers and aldehydes were 0 % (0 %). The acids and esters were calculated as 6.59 % (1.86 %). The alkanes and alkenes were 24.2 % (5.57 %). The N-heterocycles were 8.69 % (7.03 %).

Table 5 Relative Proportions (area%) of the Catalytic Fast Pyrolysis of Jatropha Waste Using Quartz Reactors

No.	Organic products	Area%			
		No-cat	QR-NiAC[a)]	QR-500C-NiAC[a)]	QR-800ml-NiAC[a)]
	Aromatic hydrocarbons				
1	Benzene, pentyl-		0.44	0.82	
2	Naphthalene		4.04	1.91	4.13
3	Benzene, hexyl-		0.00	0.97	
4	Benzene, (1,3-dimethylbutyl)-		0.79	0.74	
5	Naphthalene, 2-methyl-		2.23	1.55	5.69
6	Naphthalene, 1-methyl-		4.18	2.27	3.14
7	Benzene, heptyl-		1.30	1.11	1.86
8	Biphenyl		4.77	4.75	8.62
9	Naphthalene, 1-ethyl-		1.64	1.28	
10	Diphenylmethane		0.95	0.61	
12	Naphthalene, 1,7-dimethyl-		2.21	1.68	
13	Naphthalene, 1-propyl-			1.38	
14	1,1'-Biphenyl, 3-methyl-		1.60	0.65	
15	Benzene, octyl-			1.97	
16	Benzene, nonyl-		1.70	1.75	2.18
17	Benzene, decyl-				
18	Fluorene		8.32	8.15	16.8
19	Benzene, dodecyl-			1.09	
20	Benzene, (1-methyldecyl)-		3.15	3.84	5.10
21	Phenanthrene		2.30	1.58	
22	9H-Fluorene, 9-methylene-		0.49	0.41	
	Phenols				
23	Phenol	1.45	2.21	0.47	2.08
24	Phenol, 2-methyl-	1.23	0.86	0.29	
25	Phenol, 4-methyl-	2.97	3.24	1.22	
26	Phenol, 2,4-dimethyl-	1.54	0.84	0.91	
27	Phenol, 4-ethyl-	1.34	0.85		
28	Phenol, 3,5-dimethyl-		0.58	0.66	
29	Phenol, 2-methoxy-6-methyl-			0.62	
30	1,2-Benzenediol	1.99			
31	2-Naphthalenol		1.07		
	Alcohol-Ketones				
32	1H-Inden-1-one, 2,3-dihydro-		1.43		
	Acids, Esters				
33	Acetic acid	3.97			
34	*n*-Hexadecanoic acid	8.44	1.08	2.99	
35	Octadec-9-enoic acid	22.54	1.22	10.04	
36	Octadecanoic acid	4.86			
	Alkane-Alkenes				
37	Tetradecane	1.42	0.78	0.68	
38	Cyclododecene				
39	Cyclopentadecane		1.72	1.52	2.08
40	5-Octadecene, (E)-		1.93	0.92	5.00
41	9-Octadecene, (E)-		5.30	0.29	2.77
42	Pentadecane		5.12	4.61	10.40
43	1,13-Tetradecadiene		2.33		
44	8-Heptadecene		1.80	1.41	2.48
45	Heptadecane		3.20	3.28	6.41
46	1,9-Tetradecadiene		1.51		
	N-heteroatom				
47	Pyridine, 2,4,6-trimethyl-	0.44	0.51		
48	Pyrrolo[3,2-c]pyridin-4(5H)-one		0.58		
49	Quinoline + Isoquinoline		0.57		
50	Indole	1.46	3.17	1.04	
51	1H-Indole, 7-methyl-	1.29	1.39	0.91	
52	Indolizine, 6-methyl-		0.52		2.32
53	1H-Indole, 2-methyl-	0.65	0.67		
54	1H-Indole, 2,6-dimethyl-				
55	3-Pyridinecarbonitrile, 1,4-dihydro-1-methyl-		0.87		
56	1H-Pyrrole-3-carbonitrile		0.93		

(continued on next page)

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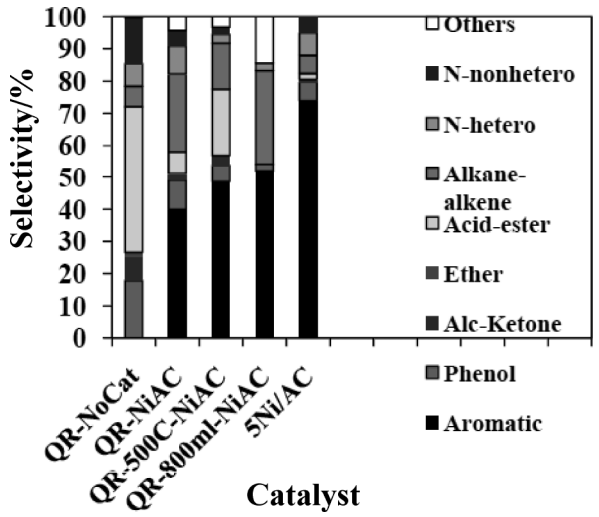
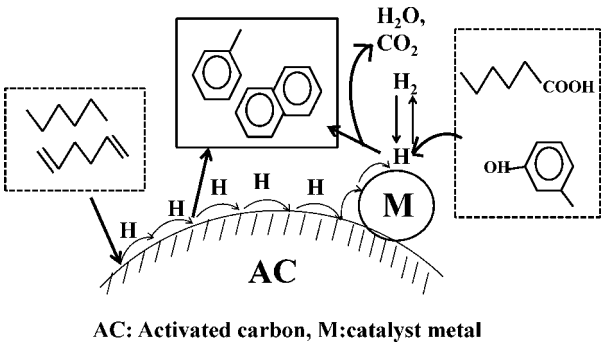
No.	Organic products	Area%			
		No-cat	QR-NiAC[a)]	QR-500C-NiAC[a)]	QR-800ml-NiAC[a)]
	N-nonhetero				
57	Benzyl nitrile	1.97	1.43	0.34	
58	Benzenepropanenitrile	0.61	0.90	0.41	
59	Benzonitrile, 2,4,6-trimethyl-				
60	Hexadecanenitrile	0.43		0.41	
61	Octadecanenitrile		1.33		

a) QR denotes quartz reactor. NiAC denotes Ni/C catalyst. 500C denotes reaction temp. at 500 ℃. 800ml denotes N_2 = 800 mL/min.



For comparison, Ni/C data obtained from Py-GC/MS is also given.

Fig. 7 Relative Selectivities from GC/MS Analysis of Bio-oil Obtained by Pyrolysis in Fig. 6



AC: Activated carbon, M:catalyst metal

Fig. 8 Postulated Reaction Scheme over Activated Carbon Surface

The N-nonheterocycles such as benzylnitrile and octadecanenitrile were 4.75 % (5.01 %). The difference in selectivity between Py-GC/MS and reactor runs might depend on the different waste/catalyst weight ratio of 0.16 for Py-GC/MS compared to 2 for the reactor, and the different scale of 0.4 mg for Py-GC/MS compared to 10 g for the reactor. These findings suggest that the use of a quartz reactor could form compounds other than aromatics more favorably under these conditions.

As shown in **Table 3**, phenol derivatives and aliphatic oxygenates are predominantly formed in the fast pyrolysis without catalyst, whereas aromatic hydrocarbons are increased by adding activated carbon catalyst, and the aromatic selectivity is further increased by use of Ni- or Mo-modified activated carbon catalyst. Therefore, we speculate that, in the presence of metal-modified activated carbon catalyst, successive reaction through hydrogen migration effect[10)] could occur at 550-600 ℃, as shown in **Fig. 8**. The aliphatic paraffins and olefins undergo dehydrogenation and aromatization to give aromatic hydrocarbons. Hydrogen formed could migrate over the activated carbon surface to reach the metallic surface, and metal-activated hydrogen caused acceleration of the hydrodeoxygenation (HDO) of the aliphatic oxygenates and phenols to form aromatic hydrocarbons. These suggestions are consistent with **Figs. 4** and **7**. The hydrogen migration nature of metal-modified activated carbon catalyst would further favor progress of these multi-steps. Selectivity for phenols and aliphatic acids were 31.4 % and 31.9 % for the Fe/C or Co/C catalysts, respectively, much larger than 7.68 % for Ni/C and 1.78 % for Mo/C. These findings indicate that the hydrogen migration ability of the activated carbon catalyst surface is, possibly, retarded by Fe or Co modification. As a result, aromatic selectivities for these two catalysts were lower than that of activated carbon, as shown in **Table 3**.

Further work is in progress to increase aromatic hydrocarbon yields under lab-scale reactor conditions as well as under Py-GC/MS conditions.

4. Conclusions

Catalyst synthesis, screening, and testing using Py-GC/MS and a quartz reactor were carried out to investigate the pyrolysis of Jatropha waste. Py-GC/MS analyses revealed that activated carbon supports were effective, with more efficient Ni/C catalyst producing 79.4 % aromatic and aliphatic hydrocarbons. In runs using a quartz reactor, selectivity for aromatic and aliphatic hydrocarbons was 64.1 %, with N-containing products generated at 13.4 %, showing the selectivity

for hydrocarbons was a little lower in the quartz reactor than that in the Py-GC/MS run. We conclude from these results that economical activated carbon-based catalysts, especially impregnated with Ni, are good candidates for fast pyrolysis of Jatropha waste with acceptable capacity to deoxygenate pyrolysis vapor at 600 ℃, resulting in a liquid product with appreciable amounts of aromatic and aliphatic hydrocarbon species but little oxygen in their structures. We speculate that, in the presence of metal-modified AC catalyst, successive reaction through the hydrogen migration effect occurs at 600 ℃. The difference in the hydrocarbon selectivity between the Py-GC/MS and reactor experiments could be due to the experimental conditions, such as the sample/catalyst ratio and reactor configuration. Modification of the reactor, combined with catalyst improvement, is required to scale up the process to produce liquid fuel commercially from this non-edible plant.

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要　　旨

ジャトロファ搾油廃材の急速熱分解に対する金属修飾炭素触媒の効果

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熱分解 GCMS，石英反応管などを用いて，ジャトロファ搾油廃材の急速熱分解のための金属修飾炭素触媒の探索を行った。熱分解 GCMS を用いた結果から，含浸法で Ni を修飾した活性炭（AC）触媒が有効であることを見出した。主生成物は芳香族または脂肪族炭化水素であり，合計選択率は79.4 %，含酸素化合物などが副生した。Ni ／活性炭触媒を用いて石英反応管で反応させた時，芳香族および脂肪族炭化水素選択率は熱分解 GCMS 法より少し低く 64.1 % であった。Ni ／活性炭触媒上での水素移動を通して，逐次反応が 600 ℃ で起こっていることを推定した。商業規模で液体燃料製造プロセスを構築するためには，触媒性能そのものや反応方法などの改良がさらに必要であることが分かった。

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