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An Efficient Utilization of Inedible Fruit for Fossil Substitution

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Because the jatropha fruit gives a high yield of oil and has been expanded in many regions, it was selected as a representative of the inedible fruits and was investigated as a multipurpose biomass to be converted to various kinds of fuels and chemicals equivalent to those from fossil resources. Specifically, in this study, the biodiesel and activated carbon were prepared from its oil and shell, respectively. Although crude jatropha oil contained a higher amount of free fatty acid, this acid could be removed prior to alkali transesterification resulting in improvement of the overall biodiesel yield. The transesterification yield of biodiesel from the crude jatropha oil (CJO) was similar to that from used frying oil (UFO), and greater than that from crude palm oil (CPO), which would be attributed to relatively low C_{16}/C_{18} ratio in the CJO and UFO. The jatropha shell was successfully converted into activated carbon by thermal treatment under either steam or inert atmosphere. The impregnation, particularly with potassium hydroxide, prior to thermal treatment under inert atmosphere provided the activated carbon with a greater porosity comparable to those obtained under steam atmosphere without impregnation. The obtained activated carbon was expected to be utilized in the purification of glycerol, the by-product of biodiesel production, to enhance the feasibility of the biodiesel production.

1. Introduction

In the past few decades, the over-use of fossil resource as mono-energy in transportations and industries had been leading to not only energy crisis but also many environmental concerns. To solve this problem, the renewable-clean energies such as the synthesis fuel from biomass have been promoted around the world as the alternative approach for the replacement of fossil fuels demand. Furthermore, in view of biomass utilization, such a raw biomass should efficiently substitute for several kinds of fuels and chemicals as much as those derived from the fossil resources. Taking into account the biomass resource, basically, it can be mainly divided into three categories; edible biomass, inedible biomass, and waste. The biosynthesis from waste sounds the most economically among the three kinds of biomass since the waste is considered as the costless feedstock; however, the biosyntheses from the two former biomasses are beneficial on reduction of carbon dioxide as so-called carbon neutral. However, the

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escalating expansion of edible biomass consumption for fossil resources substitution purpose causes the depletion of food supply and economic imbalance. In this context, the biosynthesis from inedible biomass, which could reduce the carbon dioxide emission as well as did not reduce the security of food supply, would be more interesting, and the appropriate method of its value added process should be empirically investigated.

Jatropha fruit is one of these inedible biomasses. Since this fruit gives a high yield of oil and can grow in the wide range of climate and soil, it attracts much attention as a multipurpose raw biomass to produce the valuable fuels and chemicals.

In this study, we tried to synthesize a process complex converting jatropha fruit. Firstly, biodiesel production from crude jatropha oil was examined under various conditions. This result was compared with those from crude palm oil as an edible oil and from used flying oil as a waste. These comparisons are necessary also for the improvement of the feed oil flexibility to overcome insufficient feed supply in biodiesel production. Secondly, activated carbon was obtained by thermal treatment of the jatropha shell, which is a new raw material for activated carbon. Based upon these experimental results, the process integration of biodiesel production and biomass thermal treatment was discussed in terms of the feasibility of biomass substitution for fossil fuels and chemicals.

2. Experimental

2.1 Biodiesel production from crude jatropha oil

Crude jatropha oil (CJO) was obtained from Thailand, while crude palm oil (CPO) and used flying oil (UFO) were obtained from Malaysia and Japan, respectively.

Before the transesterification, the feed oil was pretreated (feed pretreatment, FP) to remove unfavourable impurities, such as free fatty acid (FFA), phosphatide, and moisture, which not only contaminate the biodiesel product but also deactivate catalyst and reduce the production yield. FFA was neutralized with sodium hydroxide, NaOH, (deacidification, DA), phosphatide was solubilized into water by phosphoric acid, and moisture was adsorbed on magnesium sulphate.

The feed oils before and after pretreatment were characterized in terms of fatty acid radical composition, acid value, phosphatide, and moisture contents. After the feed oil was treated to completely convert triglycerides in the oil into methyl ester of each fatty acid, it was analyzed by a gas chromatograph (GC) to determine the fatty acid composition in the feed oil. Acid value of the oil was obtained by titration according to ASTM D 664. The average molar mass of fatty acid and triglyceride in the feed oil were calculated from the content of FFA and the composition of oil. The content of

Table 1 Principal experimental conditions for transesterification

Feed oil	pretreated CJO, CPO, UFO
Mass of feed oil [g]	15
Alcohol (methanol)/ feed oil molar ratio, M [–]	3-9
Catalyst (NaOH)/ feed oil mass ratio, C [–]	0.005-0.015
Reaction temperature [K]	333
Reaction time [h]	1

phosphorus from phosphatide in the feed oil was determined by using an inductively coupled plasma spectrometer. Moisture content in the oil was measured by a Karl-Fisher titrator.

The principal experimental conditions for transesterification of all kinds of feed oils are shown in Table 1. The reaction was carried out in a 50×10^{-6} m^3 three-necked flask, which was equipped with reflux condenser. The alcohol (methanol)/oil molar ratio and catalyst (sodium hydroxide, NaOH) concentration were varied to investigate the effects of these variables on the biodiesel purity and production yield. After transesterification, the mass and the methyl ester composition of biodiesel, the lighter liquid phase of the products, was measured (Dhruv et al., 2004).

The methyl ester contents in the biodiesel were determined by analyzing the biodiesel directly by the GC (Sinthupinyo et al., 2008a).

2.2 Activated carbon preparation from jatropha shell

The jatropha shell sample after removing the seed, which was procured from Thailand, was washed with deionized water, dried in the oven at 378 K for 24 hours, then crushed, and sieved to the desired size.

The element composition in the shell sample was determined by the ultimate analysis using CHNS/O analyzer. The volatile matters, fixed carbon, and ash content in the sample were determined by proximate analysis using thermogravimetric analyzer (TGA).

In some runs, the dried sample was impregnated in 10 wt% concentration of potassium hydroxide or phosphoric acid aqueous solution with the mass ratio of solution/sample equal to 1.0 for 24 hours, the solution was decanted off, and the sample was dried in the oven at 378 K for 24 hours, before thermal treatment. The principal experimental conditions for thermal treatment are shown in Table 2. A horizontal stainless steel tubular-reactor with thermocouple inserted into electrically heating furnace with temperature controller was used as a pyrolyzer. The particle size, impregnation chemicals, pyrolysis temperature, and atmosphere were systematically varied. The principal range of pyrolysis temperature was obtained from the range in which significant mass loss occurred according to the TGA result. After the prepared activated carbon (AC) was boiled with deionized water at 373 K for two hours, it was dried in the oven at 378 K for 24 hours, powdered, and stored in the desiccator.

The BET surface area (A_{BET}), total pore volume (V_{total}), and micro pore volume (V_{micro}) of the obtained AC are determined from an isotherm of nitrogen adsorption (Sinthupinyo et al., 2008b).

Table 2 Principal experimental conditions for thermal treatment

Feed	jatropha shell
Particle size [mm]	<0.35, 0.425~1.7, 25-30[a]
Mass of feed [g]	approx. 20
Atmosphere	N_2, H_2O
Flow rate of atmospheric gas [$m^3 \cdot h^{-1}$]	
Nitrogen	0.03
Steam	0.24×10^{-4}
Temperature [K]	423~923
Holding time [h]	0.5

3. Results and Discussion

3.1 Biodiesel production from crude jatropha oil

The feed oils characterization revealed that CJO contained the highest content of phosphatide, FFA, and moisture, and the oleic acid (C_{18}) was found as the main fatty acid in CJO. In fact, all of feed oils similarly contained fatty acids mainly of C_{16} (palmitic acid) and C_{18} (stearic acid, oleic acid and linoleic acid), though CJO and UFO had relatively lower C_{16} chains than CPO. The FFA was considered as the most significant impurity since the CJO would be converted to jelly-soap instead of biodiesel unless DA was carried out. Lastly, the impurities in CJO could be reduced comparable to those in CPO and UFO after it was appropriately treated in FP; nonetheless, a feed loss, particularly in DA was remarkable due to the saponification of triglyceride during neutralization with NaOH.

Figure 1 depicts the effects of methanol and NaOH amounts on purities or the mass fractions of methyl ester, x_{ME}, and yields in transesterification, Y_{ME}, of biodiesel, with full feed pretreatment. The x_{ME} in the case of CJO was greater than that of UFO but lower than that of CPO. This maybe because CPO has the relatively higher content of C_{16} fatty acid, the shorter chain of which the unreacted diglyceride and monoglyceride could be dissolved in the glycerol/aqueous phase superior to those with longer chain, and finally contaminated the biodiesel product. On the other hand, CJO and UFO, which contained the longer chain tended to give the greater Y_{ME}; it had been reported that low-molecular weight oil had higher saponification value and was converted into soaps more. Not only triglyceride was unfavourably consumed by the soap formation instead of transesterification, but also the formed soap lowers the reaction rate by foaming with gas in the reactor and interferes the separation between methyl ester and glycerol. The effects of C and M were similar for all kinds of oils; the maxima of x_{ME} were found with increasing C or M, while the Y_{ME} had a maximum over C but increased with M (Sinthupinyo et al., 2008a).

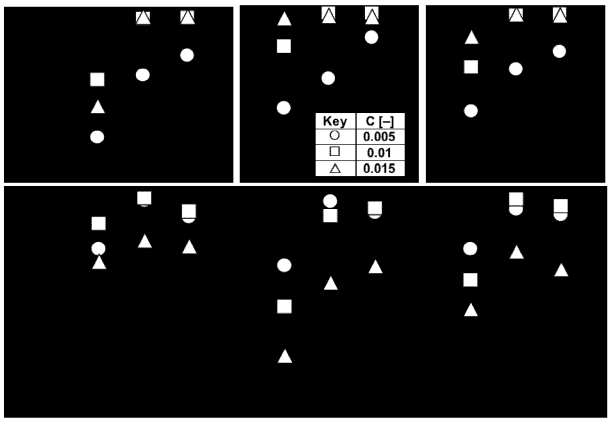

Figure 1 Effects of methanol and NaOH amounts on biodiesel purities, x_{ME}: (a) CJO; (b) CPO; (c) UFO; and yields, Y_{ME}: (d) CJO; (e) CPO; (f) UFO

3.2 Activated carbon preparation from jatropha shell

It could be predicted from the results of ultimate and proximate analyses of jatropha shell as summarized in Table 3 that the AC derived from jatropha would tend to give low yield of AC but superior in surface area due to relatively low fixed carbon and high volatile matters contents, and also high oxygen content would promote the formation of porous structure.

It was observed that the larger particle size resulted in greater gas and solid yields but lower liquid yield. On the contrary, the smaller particle size led to improvement of the A_{BET}, V_{total} and V_{micro} (Sinthupinyo et al., 2008b).

The effects of pyrolysis atmosphere and temperature on distribution of products yield together with the AC characteristics were shown in Figure 2. The solid yield continually decreased as temperature increased up to 923 and 1023 K under steam and nitrogen, respectively. In the case of steam, char gasification would become the dominant reaction above 773 K as seen from significant increase in gas yield and decrease in char yield at 923 K. On the other hand, in the case of nitrogen, the formation of gas from the secondary reactions of tar would be the dominant reaction at 923 K, so that liquid yield decreased, gas yield increased, and there was no change in char yield. Unlike that of steam, the char gasification under nitrogen would occur at temperature higher than 923 K, as evidenced by increase in gas yield, decrease in solid yield, and constancy of liquid yield. The liquid yield from both under steam and nitrogen increased with temperature and the maxima were found at 773 K. The gas yields in the case of steam were always higher than those of nitrogen due to reaction of water such as water-gas shift reaction and steam-hydrocarbon reforming. The A_{BET}, V_{total} and V_{micro} increased with temperature under either steam or nitrogen, and they were quite similar in both cases up to 773 K over which char gasification was the dominant reaction leading to significant increase in A_{BET} in the case of steam. The AC porosity in the case of steam was superior to that of nitrogen because of the extent of steam reforming.

Table 3 Ultimate and proximate analyses of jatropha Shell

Ultimate analysis (wt%)				Proximate analysis (wt%)		
C	H	N	O	Volatile matter	Fixed carbon	Ash
43	6	1	50	90	0	10

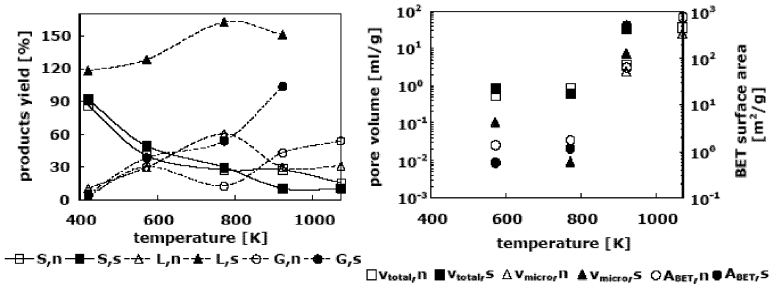

Figure 2 Effects of Pyrolysis Atmosphere and Temperature on Products Yield and AC Characteristics; S:solid, L:liquid, G:gas, s:steam atmosphere, n:nitrogen atmosphere

The chemical impregnation showed that the solid yield could be improved by phosphoric acid and potassium hydroxide impregnation, respectively. In addition, the A_{BET} and V_{total} were improved by the chemical impregnations particularly with potassium hydroxide, which reached maximum 520 m^2/g at 923 K (Sinthupinyo et al., 2008b).

3.3 Process integration of biodiesel production and activated carbon preparation from jatropha fruit

In a general transesterification process, about 10% of feed oil will be converted to crude glycerol, which is the main by-product of biodiesel production containing a traces amount of methanol, water, and fatty acids. The purification process to remove these impurities including color and odor is a crucial step to obtain a high-grade glycerol, which is highly required in food, pharmaceutical and cosmetic industries. Typically, the adsorption by activated carbon is well-established technology in this final glycerol purification process; nevertheless, the activated carbon is expensive, bulk consumed, and its application causes the extraordinary production cost. In this sense, the process integration of activated carbon prepared from jatropha shell waste thermal treatment as investigated in this study into the biodiesel production is considered as an alternative approach to reduce the purchased activated carbon as well as undertake value added jatropha shell waste resulting in enhancement of biodiesel feasibility. Furthermore, in more general, it could substitute for the existing activated carbon derived from natural coal, a non-renewable resource, which should be prolonged for future generations.

4. Conclusion

The jatropha fruit successfully performed as the multipurpose raw biomass for the fossil fuels and chemicals substitution. The biodiesel produced from crude jatropha does not overhang the food market, and its yield and purity were comparable to those from crude palm oil and used flying oil. Indeed, its transesterification yield was greater than that of crude palm oil by applying the appropriate feed pretreatment corresponding to its impurities. The high surface area-activated carbon could also be prepared from the jatropha shell by either the thermal treatment under steam atmosphere or potassium hydroxide impregnation followed by nitrogen atmospheric thermal treatment. The utilization of the prepared activated carbon in the purification of glycerol in the biodiesel production process would improve the biodiesel profitability as well as the activated carbon would be substituted for that derived from natural coal in general.

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