

Utilization of Byproducts in the Process of Biodiesel Production from Jatropha

Student Number: 08M18134

Name: Tomoki HAYASHI

Supervisor: Ryuichi EGASHIRA

ジャトロファ由来バイオディーゼル燃料製造プロセスにおける副生成物の利用 林 知輝

まず、粗ジャトロファ油を、前処理後、メタノールとエステル交換することによりバイオディーゼル燃料およびグリセリン(副生成物)を作成しこれらを分析した。粗グリセリンの収率は約 0.23 と一定値であり、理論的なグリセリンの生成量と未反応メタノールの和に等しい。グリセリン中には未反応メタノールと中間生成物であるモノオレインが含まれるため、各々濃度を測定した。ついで、油脂圧搾後のジャトロファ殻(副生成物)を熱処理し活性炭を作成した。熱処理前のジャトロファ殻の化学処理や熱処理における水蒸気雰囲気の利用などにより表面積および細孔容積は増加した。さらに、上記で得られたジャトロファ殻活性炭を用いてメタノールおよびモノオレインの不純物を含むグリセリン溶液の平衡吸着を行った。ジャトロファ殻活性炭はグリセリン中の不純物を良好に吸着した。グリセリンの精製に十分な活性炭量が得られたことを確認した。

1. Introduction

The jatropha fruit is a promising biomass especially for the biodiesel production as its kernel-oil (crude jatropha oil, CJO) is inedible and has no competition with food oils. The utilization of CJO could contribute to the concerns over the economic imbalance and destruction of ecosystem.

In transesterification glycerol is produced as byproduct. In current glycerol market high purity glycerol is required. In order to remove color and trace impurities from crude glycerol adsorbent such as activated carbon, ion exchange resins and molecular sieves are used. After jatropha seed is removed for biodiesel production, the shell approximately 40% of the fruit is remained and it may initiate the waste problem. A more viable option would be conversion of this shell waste into value added product, for example thermal treatment of shell waste to produce activated carbon.

This dissertation tried to utilize byproducts in biodiesel process. Transesterification of CJO was carried out to obtain biodiesel and glycerol and to measure composition of glycerol. Thermal decomposition of jatropha shell was conducted to obtain activated carbon. The yield and characteristics of the activated carbon were estimated. Adsorption experiment was carried out to confirm the feasibility of glycerol purification by the activated carbon from jatropha shell.

2. Transesterification of crude jatropha oil

2.1 Experimental

Feed oil

The compositions of feed oil and other plant oils are summarized in **Table 2.1**. CJO and model jatropha oil (MJO) was selected as feed oil in this study. The MJO was made of a mixture of tripalmitin (C_{16}) and triolein (C_{18}).

Feed pretreatment

Since CJO contained high amount of free fatty acid, the feed pretreatment (FP) is necessary before transesterification. FP removes phosphatide (degumming, DG), FFA (deacidification, DA), and water (drying) from

feed oil. Two methods of DA were used: one was alkali neutralization (ALDA) and the other was acid esterification (ACDA). The procedure of FP was same as previous works¹⁻².

Transesterification

The experimental conditions in the transesterification are summarized in **Table 2.2**. The mixture of methanol and catalyst (sodium hydroxide) were added to the pretreated oil. The transesterification is a set of simultaneous reactions and is heterogeneous during reactions. Therefore, the liquids in the reactor were well mixed by a magnetic stirrer. The pretreated oils were transesterified to fatty acid methyl ester (biodiesel) and glycerol.

Purification of biodiesel and glycerol

Biodiesel was washed by water. Crude glycerol was washed by H_3PO_4 aq to remove salt (soap) then methanol was vaporized at 378K for 0.5hr.

Table 2.1 Compositions of Jatropha oil and other plant oils

Plant oil	Fatty acid composition				
	14:0	16:0	18:0	18:1	18:2
Jatropha	0	0.103	0.138	0.427	0.263
Palm	0.011	0.350	0.046	0.421	0.166
Corn	0	0.117	0.019	0.252	0.606
Cottonseed	0	0.283	0.009	0.133	0.575
Peanut	0	0.114	0.024	0.483	0.320
Rapeseed	0	0.035	0.009	0.644	0.223
Soybean	0	0.118	0.032	0.233	0.555
Sunflower	0	0.061	0.033	0.169	0.737

Table 2.2 Experimental conditions in transesterification

MeOH/oil molar ratio	[-]	6
NaOH/oil mass ratio as catalyst	[-]	0.01
Reaction temperature	[K]	333
Reaction time	[h]	1

2.2 Results and Discussion

The yield of pretreated oil in FP (Y_{PO}), the yield of each product (biodiesel and crude glycerol) in transesterification (Y_{BDF} , Y_{CG}), and overall yield of each product in whole biodiesel production ($Y_{O.A.BDF}$, $Y_{O.ACG}$) were defined as,

$$Y_{PO} = \frac{M_{PO}}{M_{FO}} \quad (1) \quad Y_i = \frac{M_i}{M_{TO}} \quad (2) \quad Y_{O.A,i} = Y_{PO} \times Y_i \quad (3)$$

Figure 2.1 shows the effect of DA method on the

yield in FP. Y_{PO} steeply decreased with $x_{FFA,0}$ in the case of ALDA, since the saponification of triglyceride was more remarkable with larger amount of NaOH used for the deacidification²⁾. In the case of ACDA, Y_{PO} 's were higher than those in the case of ALDA.

The Y_{BDF} and Y_{CG} are plotted against $x_{FFA,FP}$ in Fig.2.2. Y_{BDF} 's were almost constant at about 1. Y_{CG} was close to 0.23, which value equaled to theoretical amount of glycerol plus unconverted methanol in transesterification in this study. The method of DA did not influence Y_{BDF} and Y_{CG} .

The overall yields in biodiesel process are shown in Fig.2.3. The method of DA influenced both $Y_{OA,BDF}$ and $Y_{OA,CG}$ strongly. Triglyceride loss in ALDA was larger than that in ACDA.

Table 2.3 shows the compositions of crude and purified glycerol. Unreacted alcohol and intermediate glyceride especially monoglyceride are remained in glycerol. In this study methanol and monoolein were analyzed since methanol was used in transesterification and triolein was the highest mass fraction in CJO. By alkali removal and methanol removal, amounts of salt and methanol were reduced. Mass fractions of alcohol and monoglyceride in glycerol have to be less than 0.00002 and 0.0005, respectively. More purification process such as adsorption by activated carbon is necessary.

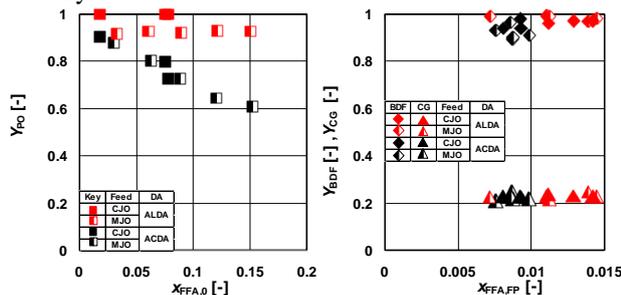


Fig.2.1 Yield of pretreated oil in deacidification

Fig.2.2 Yield of biodiesel fuel and crude glycerol in transesterification

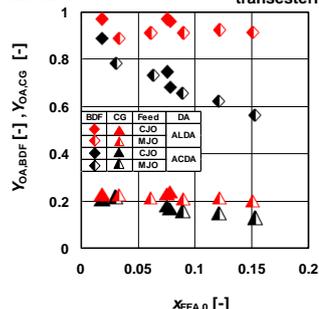


Fig.2.3 Overall yield of biodiesel fuel and crude glycerol in whole biodiesel production

Table 2.3 Compositions of glycerol

	Mass fraction [-]		
	Methanol	Monoolein	Glycerol
Crude glycerol	0.374	0.014	0.55
Purified glycerol	0.001	0.019	0.98

3. Thermal treatment of jatropha shell

3.1 Experimental

The compositions of jatropha shell and other

biomasses are summarized in Table 3.1. In order to compare with other biomass, palm shell was also used as biomass feedstock. The jatropha shell and palm shell was washed with deionized water, dried at 378K for 24hr, crushed and sieved from 0.425 to 1.7mm. As option, the shells were impregnated in 10wt% KOH or H_3PO_4 solution for 24hr, then filtrated and dried before thermal treatment. KOH or H_3PO_4 are generally used as alkali and dehydration reagent, respectively. Table 3.2 shows the experimental conditions in thermal treatment. The shells were thermally treated varying experimental conditions, such as thermal treatment atmosphere (nitrogen (n), steam (s)), and thermal treatment temperature. Solid products (char) from thermal treatment and commercial activated carbon (charcoal, Activated, Powder; Wako chemical) shown in Table 3.3 were analyzed to measure BET surface area and pore volume.

Table 3.1 Chemical compositions of Jatropha shell and other biomasses

Material	Ultimate analysis [wt%]				Proximate analysis		
	C	H	N	O	Volatile	Fix-C	Ash
Jatropha shell ³⁾	43.13	5.53	1.33	50.01	90.26	0	9.74
Jatropha husk ⁴⁾	N/A	N/A	N/A	N/A	71.04	24.99	3.97
Palm shell ⁵⁾	47.6	5.38	0.66	41.38	72.7	23.6	3.6
Palm fiber ⁵⁾	46.64	5.66	1.73	39.46	73.7	12.6	6.6
Palm kernel ⁵⁾	41.47	5.77	3.00	43.49	80.3	10.3	3.2
Brazil nut shell ⁶⁾	50.0	5.8	0.7	43.5	76.1	22.2	3.6
Coconut shell ⁷⁾	47.00	6.06	1.02	45.92	79.9	18.2	1.9
Bagasse pitch ⁷⁾	48.96	6.77	0	44.27	86.0	10.8	3.2
Molasses ⁷⁾	59.22	7.48	0.08	33.21	75.4	20.6	4

Table 3.2 Experimental conditions in thermal treatment

Feed	Jatropha shell, Palm shell	
Mass of feed	[kg]	0.03-0.04
Particle size	$[\times 10^{-3} \text{ m}]$	0.425-1.7
Impregnation reagent		KOH, H_3PO_4
Temperature	[K]	423-1073
Holding time	[h]	0.5
Atmosphere		Steam, Nitrogen
Pressure	[atm]	1
Steam flow rate	$[\text{m}^3/\text{h}]$	0.03
Nitrogen flow rate	$[\text{m}^3/\text{h}]$	0.003 (Steam atm.) 0.002 (Nitrogen atm.)

Table 3.3 Experimental conditions in thermal treatment

Run No	Feed	Pyrolysis Condition		
		Temp.[K]	Atm.	Impregnation
1	Jatropha	923	Steam	w/o
2	Jatropha	1073	Nitrogen	w/o
3	Jatropha	923	Nitrogen	KOH
4	Jatropha	923	Nitrogen	H_3PO_4
5	Jatropha	1073	Nitrogen	H_3PO_4
6	Palm	923	Steam	w/o
7	Jatropha	923	Nitrogen	w/o
8	Commercial activated carbon (CAC)			

3.2 Results and Discussion

The yield of each product in thermal treatment was expressed as,

$$Y_i = \frac{M_i}{M_{BF}} \quad (4)$$

In the case of steam atmosphere, the liquid product included steam.

The yield of solid product (Y_S) is shown in Fig. 3.1. The Y_S decreased with increasing the treatment

temperature due to the high consumption of the carbon. The Y_S with impregnation was higher than that of without. For the activation with H_3PO_4 , the Y_S increased with temperature in the range of less than 800K. H_3PO_4 worked as dehydrogenation reagent and promoted porosity of carbon structure. For carbonization above 800K, the cross-section structure reached its thermal limit and a lot of bond cleavage was produced. With KOH impregnation, the Y_S decreased with temperature. Alkalis such as KOH were able to interact with carbon atoms and thus catalyze the dehydrogenation and oxidation reaction, leading to the suppression of tar evolution and development of porosity.

The yield of liquid product (Y_L) is shown in Fig.3.2. The liquid product was composed of the volatile components from biomass and the water from the feed steam. The Y_L in steam atmosphere was higher than that in nitrogen atmosphere. The Y_L decreased with temperature in the range of more than 800K. Tar were decomposed into solid and gas.

Figure 3.3 shows the yield of gaseous product (Y_G). The Y_G increased with temperature. In the case of steam atmosphere, more char and steam were reacted and more gaseous product was produced with higher temperature. The H_3PO_4 impregnation provided higher liquid yield than KOH impregnation, whereas the KOH impregnation provided high gas yield.

Figure 3.4 shows char characterization: BET surface area and pore volume. BET surface area and pore volume were higher with temperature. With impregnation, BET surface area and pore volume were much higher than those without impregnation.

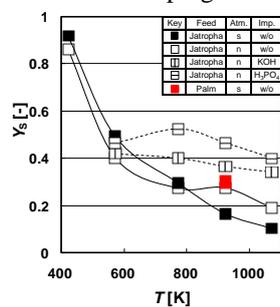


Fig.3.1 Yield of solid product in thermal treatment

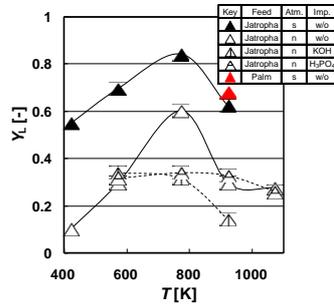


Fig.3.2 Yield of liquid product in thermal treatment

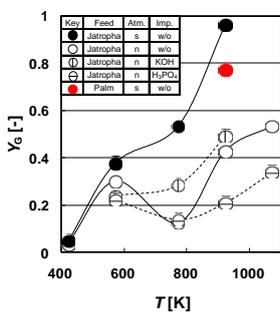


Fig.3.3 Yield of gaseous product in thermal treatment

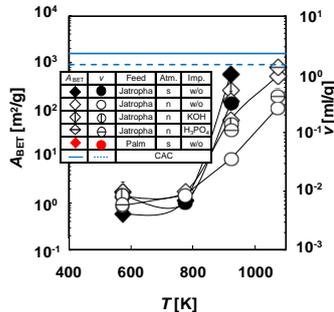


Fig.3.4 BET surface area and pore volume of char

4. Purification of glycerol using activated carbon from jatropha shell

4.1 Experimental

The char from jatropha shell, and palm shell were used as adsorbent. Also the commercial activated carbon

was used to confirm whether the char could be useful as activated carbon. The experimental conditions of adsorption are summarized in Table 4.1. The char was mixed with various concentrations of model glycerol solution with methanol or monoolein and the mixtures were put in the shaker at 303K for 72hr enough for the adsorption equilibrium. Methanol and monoolein were selected as unconverted alcohol and intermediate glyceride in transesterification. After the adsorption experiment, the glycerol solution was separated from the char by filtration. The initial and equilibrium concentration of glycerol solution were analyzed.

I proposed an improved biodiesel process utilizing the thermal treated product and the purified glycerol as shown Fig 4.1. CJO of 1ton/year is provided to obtain biodiesel and purified glycerol. 2.143ton/year of jatropha shell is treated to activated carbon and used for glycerol purification⁸⁾. The amount of adsorption in order to purify glycerol was assumed the saturated amount of adsorption.

Table 4.1 Experimental conditions of adsorption

Feed	Glycerol solution of methanol or monoolein
Mass of feed [kg]	20×10^{-3}
Mass fraction of methanol or monoolein [-]	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$
Adsorbent	Activated carbon from jatropha shell and palm shell Commercial activated carbon
Mass of adsorbent [kg]	0.2×10^{-3}
Shaking amplitude [m]	0.04
Shaking frequency [h^{-1}]	5400
Contacting time [h]	72
Contacting temperature [K]	303

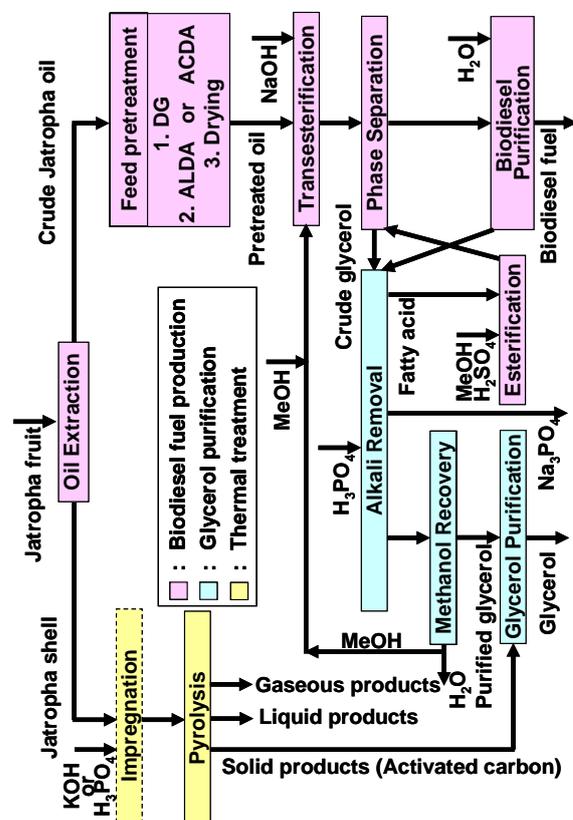


Fig.4.1 Proposal biodiesel process

4.2 Results and Discussion

The adsorption amount of each adsorbent was calculated by this material balance equation,

$$q_i = \frac{(x_0 - x_e) M_{sol}}{M_{AC}} \quad (5)$$

Figure 4.2 shows the adsorption isotherms of methanol by the activated carbon. **Figure 4.3** shows the adsorption isotherms of monoolein. Lines in the figures were plotted by Langmuir isotherm equation. The amount of adsorption of each chemical increased with temperature of thermal treatment. The Langmuir isotherm equation was used to quantify the saturated amount of adsorption. Saturated amount of adsorption of each adsorbate increased with BET surface area. These relationships are shown in **Fig.4.4** and **Fig.4.5**.

The capacity of activated carbon for methanol and monoolein ($Y_{AC} \cdot q_i^*$) is plotted against the yield of methanol or monoolein in purified glycerol ($Y_{PG,i}$) in **Fig.4.6**. $Y_{PG,i}$ was mass ratio of methanol or monoolein relative to CJO. Y_{AC} was mass ratio of activated carbon relative to CJO. The diagonal line in **Fig.4.6** means that the activated carbon from jatropha shell can fully adsorb the component in glycerol. And it shows that all the plots of activated carbon are much higher than the diagonal line. Obviously the activated carbon from jatropha shell would have enough adsorption capacity for removing the yielded amount of methanol and monoolein in glycerol.

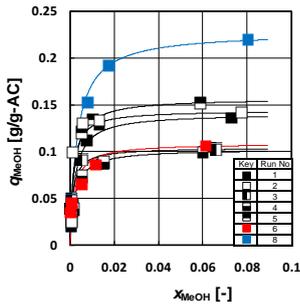


Fig.4.2 Adsorption amount of methanol

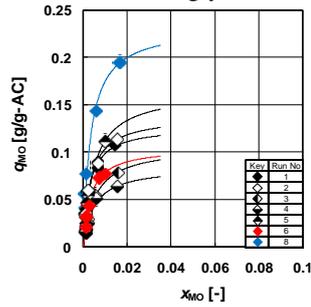


Fig.4.3 Adsorption amount of monoolein

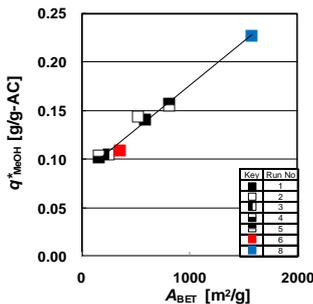


Fig.4.4 Saturated adsorption amount of methanol against BET surface area

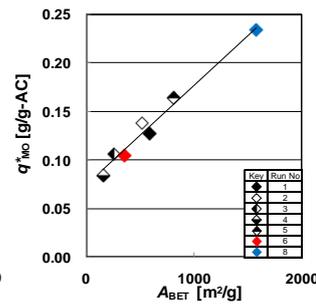


Fig.4.5 Saturated adsorption amount of monoolein against BET surface area

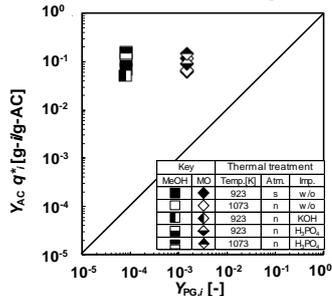


Fig.4.6 Adsorption capacity of activated carbon against yield of methanol or monoolein in glycerol

5. Conclusion

In biodiesel production yield of crude glycerol was close to 0.23. The method of deacidification influenced overall yield of products. The useful material was produced by thermal treatment of jatropha shell. Steam atmosphere and impregnation with KOH or H_3PO_4 were improved the char as activated carbon. The activated carbon from jatropha shell adsorbed impurities in crude glycerol. In overall biodiesel process there was enough amount of activated carbon from jatropha shell to purify glycerol.

Nomenclature

A	=	Surface area	$[m^2/g]$
M	=	Mass of material	$[kg]$
q	=	Amount of adsorption	$[g/g-AC]$
q^*	=	Saturated amount of adsorption	$[g/g-AC]$
T	=	Temperature in thermal treatment	$[K]$
x	=	Mass fraction	$[-]$
Y	=	Yield of product	$[-]$

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v	=	Pore volume	$[ml/g]$
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0	=	Initial state
AC	=	Activated carbon
BDF	=	Biodiesel fuel
BET	=	BET adsorption model
BF	=	Biomass feedstock
CG	=	Crude glycerol
e	=	Equilibrium state
FFA	=	Free fatty acid
FO	=	Feed oil
G	=	Gaseous product in thermal product
i	=	Component i
L	=	Liquid product in thermal product
MeOH	=	Methanol
MO	=	Monoolein
OA	=	Overall biodiesel production
PG	=	Purified glycerol
PO	=	Pretreated oil
S	=	Solid product in thermal product
sol	=	Solution
TO	=	Transesterified oil

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