P214

Approach for Transformation of Biodiesel Production Solid Residues into Value Added Products

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1. Introduction

The approach to transform the residues from biodiesel production into value added products was investigated in order to constitute more revenue into the jatropha oil based-biodiesel production. In previous studies[1, 2], the thermal treatment was carried out to convert jatropha shell, the main solid residue, into activated carbon (AC) accompanied by tar and off-gas as by-product. In this study, a techno-economic feasibility was studied to determine the appropriate thermal treatment conditions, as well as the approach of off-gas utilization.

2. Materials and Methods

The jatropha shell (JS) sample after removing the seed was obtained from Thailand. As an option, the JS was impregnated in KOH or H_3PO_4 solution, then filtered and dried before thermal treatment. The thermal treatment was carried out in the electrical tubular furnace of which the detail was described in the previous studies[1, 2]. The thermal treatment conditions considered in this study were 1) at 923K, without chemical impregnation, and under steam atmosphere (923s), 2) at 1073K, without chemical impregnation, and under nitrogen atmosphere (1073n), 3) at 923K, with KOH impregnation, and under nitrogen atmosphere (923K), and 4) at 1073 K, with H_3PO_4 impregnation, and under nitrogen atmosphere (1073H). The mass and energy balance for each condition were calculated. The economic feasibility study was categorized into four cases; case 1: stand-alone biodiesel, case 2: stand-alone biodiesel + oil extraction, case 3: stand-alone biodiesel + oil extraction + thermal treatment, and case 4: stand-alone biodiesel + oil extraction + thermal treatment + methanol synthesis. The NPV and IRR based on 10 years plant life and 3% discount rate for all cases were determined and compared.

3. Results and Discussion

The thermal treatment conditions selected for AC derived from JS were considered based on the corresponding obtained activated carbon yield and characteristics. When the impregnation was not carried out, those appropriate conditions were obtained at the temperature higher than 923 K and 1073 K in the case of steam and nitrogen, respectively. The appropriate temperature in terms of improvement in both yield and characteristics for KOH and H_3PO_4 were 923K and 1073K, respectively. The mass balances for all conditions of thermal treatment are summarized in **Table 1**. The AC yield in the case with impregnation was greater than that without impregnation. The yield of gas product in the case of steam was higher than that of nitrogen but the mass fractions of combustible gases was lower[2]. The energy balance of thermal treatment under conditions considered in this study is summarized in **Table 2**. The heat recovery was calculated from total heat combustion of H_2, CO and CH_4. Heat required, shown in Table 2, was the difference between $\Delta H_{f,out}$-$\Delta H_{f,in}$ and heat recovery, which was the outsource heat required to produce activated carbon when all off-gas was used as energy for thermal treatment.

The utilization of off-gas was considered in two categories: as energy for thermal treatment, and feed gas for methanol synthesis. For the latter case, the Hynol methanol synthesis[3] was applied. The Hynol process consists of three main units, which are thermal treatment of biomass, steam reformer, and methanol synthesis. The off-gas from thermal treatment is sent to steam reformer with the additional methane and steam to form CO and H_2. Then, the CO and H_2 rich gas is sent to methanol synthesis to convert all CO_2 and 85.5% conversion of CO to methanol.

The biodiesel production capacity and those of other corresponding products are shown in **Table 3**. The total revenue, total production cost, NPV and IRR based on production capacity, as shown in Table 3, for all cases are listed in **Table 4**. The NPV and IRR increase in the following order: case 1, 2, 3, and 4. In comparison among the conditions studied in case 3 and 4, the NPV and IRR increase in the following order: 923K, 923s, 1073H, and 1073n. In overall, a higher temperature required a less outsource heat for thermal treatment, which result in a lower total cost. Although the impregnation could improve the activated carbon yield, the NPV and IRR in the case without impregnation were greater than those of impregnations at the same temperature.

Table 1 Mass balance of thermal treatment from jatropha shell; unit: g/g JS, [-]

Conditions	In [-]		Out [-]								Loss [-]
							Mass fraction of gas product [-]				
	JS	H_2O	AC	Tar	H_2O	Gas	H_2	CO	CH_4	CO_2	
923s	1	0.81	0.23	0.06	0.51	0.76	0.035	0.328	0.011	0.626	0.26
1073n	1	0	0.23	0.07	0.17	0.42	0.031	0.729	0.109	0.132	0.11
923K	1	0	0.39	0.03	0.07	0.36	0.015	0.181	0.036	0.769	0.15
1073H	1	0	0.39	0.04	0.1	0.29	0.059	0.222	0.023	0.696	0.16

Table 2 Energy balance of thermal treatment from jatropha shell; unit: kJ/g JS

Conditions	$-\Delta H_{f,in}$		$-\Delta H_{f,out}$				$\Delta H_{f,out}-\Delta H_{f,in}$	Heat recovery	Heat required
	JS	H_2O	AC	Tar	H_2O	Gas			
923s	19.10	12.85	5.02	1.75	6.20	4.51	14.46	6.72	7.74
1073n	19.10	0	5.24	1.58	1.98	1.33	8.97	7.44	1.52
923K	19.10	0	8.36	1.13	0.82	2.49	6.30	2.10	4.20
1073H	19.10	0	10.00	0.63	1.23	1.66	5.58	3.48	2.10

Table 3 Production capacity

Product	Case	$\times 10^3$ton/yr
Biodiesel	1~4	100
Glycerol	1~4	11
Soap stock	1~4	2
Shell	2	219
Seed cake	2~4	262
Activated carbon	3~4	50(923s)
		50(1073n)
		85(923K)
		86(1073H)
Methanol	4	288

Table 4 Profitability analysis; unit: MM $US/yr

Case	Total revenue	Total cost	NPV	IRR
1	86.42	70.04	30.73	17%
2	120.78	87.19	115.11	29%
3 (923s)	162.54	131.54	45.88	13%
(1073n)	161.99	115.40	175.41	35%
(923K)	202.69	294.96	-1008.3	-
(1073H)	203.71	162.09	99.87	23%
4 (923s)	277.71	174.74	419.91	33%
(1073n)	277.15	140.47	699.57	49%
(923K)	317.86	326.50	-537.70	-
(1073H)	318.90	184.68	644.56	46%

Literature Cited

1) Sinthupinyo, P., et al., SCEJ Sendai C121 (2008)
2) Sinthupinyo, P., et al., SCEJ Hiroshima AA104 (2009)
3) Dong, Y; Steinberg, M., "HYNOL-An Economical Process for Methanol Production from Biomass and Natural Gas with Reduced CO_2 Emission", *Int. J. Hydrogen Energy*, **22**, 971-977 (1997)