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BIOFUEL FROM VEGETABLE OIL SLUDGE BY PYROLYSIS PROCESS

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VAN DINH SON THO[1], LE THI HOAI NAM[2]

[1]*Faculty of Chemical Technology, Hanoi University of Science and Technology*

[2]*Institutes of Chemistry, Vietnam Academy of Science and Technology*

ABSTRACT

The product distribution obtained from the pyrolysis of vegetable oil sludge was studied at atmospheric pressure in a fixed-bed reactor at 600°C. The experiment shows that vegetable oil sludge conversion was 74.03% by pyrolysis process. The dry gas formation of the gas is 9.4% and LPG is 16.96% and coke is 18.97%. The liquid products of the pyrolysis process have a large boiling range and it cover the range of gasoline fraction (28.78%), LCO (approximately 13.70%) and HCO (12.27%).

I - INTRODUCTION

Transportation fuels derived from renewable sources are potentially good alternatives for conventional fossil-derived fuels [1]. Bio-fuel can be obtained form biomass (e.g. pyrolysis, gasification) and from agricultural sources such as vegetable oil, cat fish, rubber seed oil, soybean oil … One of the potential sources could be able to convert to biofuel is vegetable oil sludge of vegetable oil manufacture. This sludge can not be further distilled for separation of fatty acid components because of the difficulty involved with separation and the higher separation cost. Therefore vegetable oil sludge could be utilized as a potential source in the production of liquid fuel and chemicals. Transesterification method of vegetable oil sludge could be able to convert into bio-fuel. The requirement of this method is required large amount of methanol [1]. The alternative method for the conversion of vegetable oil sludge to bio-fuel is catalytic cracking [2 - 6]. The objective of this paper is to carried out pyrolysis of vegetable oil sludge by fix bed reactor and using advanced analysis method to evaluation the product of the pyrolysis process such as dry gas, LPG gas, and liquid fraction in a boiling range of gasoline, LCO (light cycle oil) and HCO (high cycle oil). The coke formation during pyrolysis process also is mentioned.

II - EXPERIMENT

The vegetable oil sludge was obtained from the waste of Tuong An company. This is a waste of vacuum distillation process. The purpose of the distillation is to completely eliminate the free fatty acid of vegetable oil by vacuum distillation.

The composition detail of the liquid fraction of the vegetable oil sludge cracking reaction is analysed by GC-MS method (GC-HP HEWLETT 5890 PACKARD SERIES II; MS-HEWLETT 5989B PACKARD). Pyrolysis was done by MAT 5000 of Zeton-Canada. Main parameters of pyrolysis condition were described in table 1. The coke formation was in-situ evaluated by combustion with air and was quantified by CO_2 infrared analyzer (1440 Gas

Analyzer – Servomex). The gas product was collected in a brine water glass bottle and was analyzed by Refinery gas analyzer – Trace GC - ThermoElectro. The boiling distribution of the liquid product was determined by SIMDIST GC ThermoElectro system, detector FID integrated TriPlus auto-sampler [7].

The calibration gas is RGA standard of MESA International Technologies, Inc. The calibration liquid for distillation simulation is ASTM D2887 Calibration mix (RESTEK).

III - RESULTS AND DISCUSSION

Identification the composition of the vegetable oil sludge:

There are some main physical properties of the vegetable oil sludge and their value is described as below:

Acid value: 76.27 mg/g

Saponification number: 204.74 mg/g

Iodine number: 39.76

Solidification point: 40^{o}C.

It could be said that the composition of the vegetable oil sludge is 61% of triglyceride and 37% of free fatty acid and 2% impurities. In order to identification the hydrocarbon chain of the triglyceride and free fatty acid, the transesterification reaction of the sludge with methanol was carried out at 60^{o}C by the acid and sodium catalyst. After purification and water elimination, the mixture of methyl ester was analyzed by GC-MS. Their composition is shown in table 2 and it is a typical composition of vegetable oil.

Pyrolysis reaction

The main result of pyrolysis is mentioned in table 3 (Pyrolysis data). It is showed that the coke formation is about 14.55% of the oil feed and the liquid yield is 31.36% of the oil feel and the total gas volume of cracking gas obtains 1025ml. In order to identification the composition of the gas, the GC Trace GC – ThermoElectro was used and their composition is shown in table 4. The hydrogen do not observed but methane composition is about 1.41%. The gas product contains CO and CO_2 but the data can not be evaluation.

The simulation of the distillation for the liquid product of the pyrolysis process is shown in table 5. The weight percent of the liquid products that have a boiling point lower than 200^{o}C is 30.4% and it is about 36.3% for the liquid products that have a lower than 221^{o}C. The weight percent of the liquid product have a boiling point below 342^{o}C is 69.9%. The weight percent of the liquid product that have a boiling point in a range of the gasoline fraction, LCO and HCO fraction of the pyrolysis are calculated by the following formula [7].

Gasoline = [((IBP(<221^{o}C)/100)* Liquid product + (C_5,C_6 gas/Total gas)]/Oil feed }*100

LCO = {{[(IBP(<221^{o}C) – IBP(<200^{o}C))/100]*Liquid product}/oil feed}*100

HCO = {[(1-IBP(<221^{o}C))*Liquid product]/Oil feed}*100

Table 1: Pyrolysis condition

Temperature, ^{o}C	600.0
Total N_2 Flowrate (Prepurge), ml/s	50
Total N_2 Flowrate (Reaction), ml/s	5
Total N_2 Flowrate (Stripping), ml/s	25
Oil Feed Temperature, ^{o}C	50.0
Oil Feed Density @ 50.0°C, g/ml	0.8747
Actual Volumetric Oil Feed, ml	1.1600
N_2 Pre-purge Time, min	15.0
N_2 Reaction Time, sec	75
N_2 Stripping Time, min	10.0

The composition of liquid product was analyzed by GC-MS and their compositions are mentioned in table 6. It is about 46% of the liquid products are not identified by GC-MS. It could be said that the composition of hexadecanoic acid is approximately 10.91%. Although pyrolysis temperature is applied at 600^{o}C, there is quantity amount of hexadecanoic acid, which is a main composition of the feed, is not cracked. The triglyceride of the feed is strongly cracked to shorter hydrocarbon chain products such as hydrocarbon, alcohol and keton products. It should be noted that all products have a linear hydrocarbon chain structure.

Table 2: The composition of hydrocarbon chain of vegetable oil sludge

Composition	Hydrocarbon chain	Value, %
Dodecanoic axit	C_{12}:0	0.22
Teradecanoic axit	C_{14}:0	2.04
Hexadecanoic axit	C_{16}:0	47.90
7-Hexadecenoic axit	C_{17}:1	0.23
Heptadecanoic axit	C_{17}:0	0.28
9,12-Octadecadienoic axit	C_{18}:2	7.25
9-Octadecenoic axit	C_{18}:1	31.51
Octadecanoic axit	C_{18}:0	7.48
15-tetracosenoic axit	C_{24}:1	0.45

Table 3: The results of the pyrolysis

Oil Feed, g	1.0147
Themal cracking temp, ^{o}C	600.0
Oil Injection Time, sec	50
Feed density, g/ml	0.8747
Liquid product, g	0.3172
Liquid yield, %	31.262
Weight of carbon, g	0.13794
Coke, %	14.546
Gas volume, ml	1025

Based on the tables of the cracked-gas, liquids products and conversion formula, the final result of pyrolysis of vegetable oil sludge are shown in table 7. The material balance of the reaction is calculated by the quantity of the feed stock converted into gas, liquid and coke. The conversion of the pyrolysis is 56.76% and the materials balance of pyrolysis is 76.67%. The normalized results of this table were converted based on the materials balance and theoretically value (100%).

Table 4: The composition of the gas

Gas	Mole, %	Weight, of oil feed, %
2-Methyl-2-Butene	0.350	1.562
C6+	1.401	7.585
Hydrogen	0.000	0.000
Propane	0.756	2.120
Propylene	2.730	7.301
n-Butane	0.064	0.237
1-Butene + i-Butene	0.539	1.921
trans-2-Butene	0.050	0.180
cis-2-Butene	0.040	0.141
1, 3-Butadiene	0.322	1.107
n-Pentane	0.020	0.090
Trans/Cis-2-Pentene	0.286	1.277
1-Pentene	0.047	0.210
Carbon Dioxide	2.494	-
Ethylene	2.108	3.759
Ethane	1.027	1.964
Methane	1.388	1.415
Carbon Monoxide	3.195	-

Table 5: Simulated Distillation for the liquid product of pyrolysis process

Liq. Prod, IBP less than 200 °C (Wt% of Liquid Product)	30.4
Liq. Prod, IBP less than 221 °C (Wt% of Liquid Product)	36.3
Liq. Prod, IBP less than 343 °C (Wt% of Liquid Product)	69.9

Dry gas = Total (H_2, CO, CO_2, C_1, C_2 and C_2=)
LPG = Total (C_3, C_3=, iC_4, nC_4, C_4=, Propandien)
Coke = [(1.07*Carbon weight)/Oil feed]*100

Material balance = Dry gas + PLG + Gasoline + LCO + HCO + Coke

Conversion = Material balance – (LCO + HCO)

The conversion of the pyrolysis is 74.03%. The products of pyrolysis are dry gas (9.4%), LPG (9.4%), coke (18.97%) and the liquid products. The liquid have a wide boiling range and it cover the range of gasoline fraction (28.78%), LCO fraction (approximately 13.70%) and HCO fraction (12.27%).

Table 6: The formula and composition of the liquid products

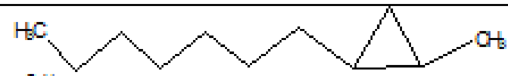
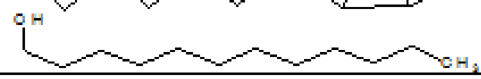
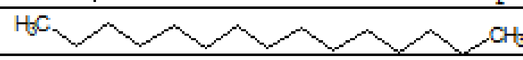
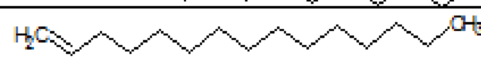
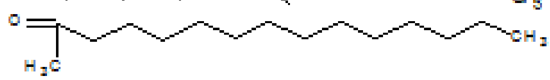
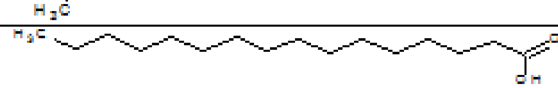
N°	Chemical	Chemical formula	%
1	1-hexyl-2-methyl-Cyclopropane		7.07
2	Dodecanol		5.79
3	1-tetradecene		9.81
4	Pentadecane		7.20
5	1-Pentadecene		5.52
6	9-Octadecene		3.32
7	2-Pentadecanone		4.34
8	Hexadecanoic acid		10.91
9	Un-identify		46.04

Table 7: The results of thermal cracking of vegetable oil sludge

Compound	WT% of feed	Normalized WT.%
H_2	0	0
C1	1.415	1.816
C2	1.964	2.561
C2=	3.759	4.903
Total dry gas	7.139	9.310
C3	2.120	2.764
C3=	7.301	9.522
n-C4	0.237	0.309
1-C4=&i-C4=	1.921	2.506
t-2-C4=&c-2-c4&1,3-butadienes	2.409	1.428
Total LPG	13.0008	16.964
Gasoline (IBP less than 221°C plus C5 in glas product	22.070	28.784
LCO (IBP between 221°C and 343°C)	10.504	13.699
HCO (IBP > 343°C plus liquid hold-up)	9.410	12.272
Coke	14.546	19.971
Conversion	56.763	74.029
Material Balance	76.677	100.000
		Normalized

IV - CONCLUSION

The pyrolysis of the vegetable oil sludge is a promising method for synthesis of bio-gas, bio-fuel from agricultural waste products. By the pyrolysis, the structure of the triglyceride is cracked and the structure of the free fatty acid also be changed. By pyrolysis, the conversion of the vegetable oil sludge is 74.03%. The products of pyrolysis are dry gas (9.4%), LPG (9.4%), coke (18.97%) and the liquid products. The composition of the liquid products is linear hydrocarbon, linear alcohol, linear keton and free fatty acid. They have a wide boiling range and it cover the range of gasoline fraction (28.78%), LCO fraction (13.70%) and HCO fraction (12.27%).

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