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REUSE OF SPENT FCC OF DUNG QUAT REFINERY FOR CRACKING WASTED COOKING OIL IN LIQUID PHASE

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Abstract

Applications of pretreated spent FCC catalyst in wasted cooking oils cracking were investigated. The spent catalyst was obtained from commercial FCC unit in Dung Quat refinery. The spent FCC catalyst was removing heavy metals by reflux with 5 % concentration solution of enthanedioic acid by magnetic stirring for 5 hours at 75 ^{o}C. The obtained results showed that 56% Fe and 30 % Ni were removed. Treated spent FCC catalyst was used in cracking wasted cooking oils in liquid phase at 370 ^{o}C, 400 ^{o}C and 420 ^{o}C for 45 minutes with rate of stirring being 400 rpm. At 400 ^{o}C liquid and gas products yield was higher than at 370 ^{o}C (82 % and 12 % in comparison with 80 % and 10 %), respectively, as a consequence, unconverted products at 400 ^{o}C were smaller than at 370 ^{o}C (2.5 % versus 6.3 %). The GC-MS results showed that the obtained products are mainly straight chain alkanes as green diesel.

Keywords. Spent FCC, regenerated FCC, green diesel, catalytic cracking.

1. INTRODUCTION

In the past few decades, fossil fuels, mainly petroleum-based liquid fuels, natural gas and coals, have played an important role in fulfilling the energy demand. However, because of their non-renewable nature, these fossil fuels are projected to be exhausted in the near future. This situation has worsened with the rapid increasing in energy demand with significant worldwide population growth, therefore, the demand for clean, reliable, and yet economically feasible renewable energy sources has led researchers to search for new sources [1]. In this respect, plant biomass is the only current sustainable source of organic carbon, biofuels, and fuels derived from plant biomass [2], such as plant oil, more commonly denoted as vegetable oils, which are castor, soybean, cotton, peanut oils, or any other vegetable oils, pure or wasted [3].

Triglycerides are the main component in vegetable oils, in which the long hydrocarbon chains in its structure are similar to crude oil. Three fatty acid chains connected via the carboxyl group to a glycerol backbone. The physical and chemical properties of vegetable oils depend strongly on their fatty acid composition [4]. Vegetable oils can be used directly in diesel engines, however, there are a number of disadvantages of pure vegetable oils, including high viscosity, low volatility and engine problems (coking on the injectors, carbon deposits, oil ring sticking…). The most common way of upgrading vegetable oils to fuel is transesterification of triglycerides into bio-diesel. Kaliaguine et al. synthesized the mesoporous silica functionalized with TBD in order to obtain the high activity catalyst in the transesterification of vegetable oil [5,6]. However, biodiesel produced by this method requires a large amount of methanol, the complex pre-processing and strict material quality [7]. An alternative option for the conversion of vegetable oils into transportation fuels might be through catalytic cracking [8].

The co-feeding of vegetable oils with fossil feedstocks to fluid catalytic cracking (FCC) units can be an interesting application [9]. Catalytic cracking method for quality of mixture products as well as mineral fuels (gasoline, diesel) and the requirements of the pretreatment process of material are less strict. Spent FCC from the Dung Quat oil refinery after regeneration is suitable for the cracking process. Most of these spent catalysts have been removed as landfill, while metals such as Ni, Fe in catalyst are hazardous wastes. Therefore, researches on the process for recycling and reutilization of spent FCC catalyst have received a lot of considerable attentions. Xin Pu et al. were successful in discarding contaminated heavy metals by using organic acid [10].

In this study, research group regenerated spent FCC catalyst deactivated partly by heavy metals such as Ni, Fe through washing with oxalic acid. The metals, mainly nickel and iron accumulated on the surface of FCC catalyst promote dehydrogenation and condensation reactions leading to enhance the formation of coke. The research group used treated spent FCC catalyst for cracking wasted cooking oils with free fatty acid factor as 67.

2. EXPERIMENTAL

2.1. Pretreatment of spent FCC

The spent catalyst was obtained from commercial FCC unit in Dung Quat refinery. Contaminated heavy metals such as Fe, Ni were removed by reflux with 5 % concentration solution of oxalic acid by magnetic stirring for 5 hours at 75 ^{o}C [10].

2.2. Characterization

The structure of FCC was characterized by XRD spectroscopy using XRD-Siemens D5005 at Hanoi University of Science. The elemental composition of FCC was determined by EDX in Hanoi University of Science and Technology.

2.3. Liquid cracking system

The reaction was carried out in the liquid cracking system at 370 ^{o}C, 400 ^{o}C and 420 ^{o}C for 45 minutes with rate of stirring was 400 r/min. The mixture reactants contained wasted cooking oils with a free fatty acid number 67 and the spent FCC after pretreatment. The ratio of FCC catalyst with wasted cooking oil is 5 wt%. The gas products were collected in a glass bottle containing brine water, the liquid products were analyzed by GC-MS. GC- MS HP 6890 with a mass spectrometry detector MS HP 5689 (American) at petroleum center- Faculty of Chemistry - HUS.

3. RESULTS AND DISCUSSION

3.1. FCC characterization

3.1.1. XRD of regenerated FCC

The XRD diffractogram shows that the major components of FCC catalyst from Dung Quat refinery contain Zeolite Y and γ- Al2O3. However in the diffractogram of regenerated FCC, some crystalline phase characterization peaks of zeolite Y were slightly shifted in comparison with the fresh FCC catalyst.

Table 1: The particular 2θ angles of original and regenerated FCC

Fresh FCC	2θ	6.3	10.5	12	15.6	18.8	20.4	23.9	27	31.5	45.6
Regenerated FCC	2θ	6.3	10.5	12	16	19	21	24	27.5	32	45.6
	d	14.102	8.954	7.328	5.586	4.672	4.303	3.699	3.247	2.813	1.987

3.1.2. EDX of spent and regenerated FCC

The EDX spectrum of spent FCC indicated that the amount of Fe, Ni accounted for large value, 3.97 % of Fe and 1.07% of Ni. The analysis results in regenerated FCC showed that the content of Fe and Ni elements was declined significantly, about 56% and 32%, respectively. The pretreatment with oxalic acid could not remove the heavy metals completely however, the presence of small amount of Ni and Fe might enhance dehydrogenation process resulting in olefins formation.

3.1.3. BET surface and micro-pore area and pore volume

BET surface and micro-pore area and pore volume of regenerated and spent FCC catalysts are summarized in table 2 to investigate the effect of regeneration process on zeolite and matrix surface area. The data of table 2 indicated that after regeneration, the porous structural data of FCC decreases noticeably, especially the BET surface area (decrease approximately 44 %). However, the size of micro-pore of regenerated FCC is well suited for the wasted cooking oil cracking.

Table 2: Surface area and pore characteristics of regenerated and spent FCC

Sample	Fresh FCC	Regenerated FCC
BET surface area (m^2/g)	211.5298	119.5154
Micro-pore area (m^2/g)	96.8410	72.9697
Micro-pore volume (cm^3/g)	0.050714	0.0384
Adsorption cumulative surface area of pores between 17-3000 Å (m^2/g)	138.163	56.157
Adsorption cumulative volume of pores between 17-3000 Å (cm^3/g)	0.295817	0.2148

3.2. The liquid-phase cracking

Table 3 describes the liquid products of catalytic cracking of wasted cooking oils which were analyzed by GC-MS method. The results showed that the main components are the derivatives of paraffinic hydrocarbon, C_{10}-C_{19}.

Nonetheless, there are some free fatty acids such as cis-9 octadecenoic acid, hexadecanoic acid still remained in the products. It can be explained by that the decarboxylation reaction did not take place completely. It can be elucidated that increasing temperature enhanced decarboxylation reaction. When the temperature rose to 420 °C the component of unconverted fatty acid went down.

Table 3: Some major components in liquid products at 370 °C, 400 °C and 420 °C

No	Nomenclature	370 °C (%)	400 °C (%)	420 °C (%)
1	Heptane (C_7H_{16})	-	-	0.77
2	Octane (C_8H_{18})	-	0.44	1.32
3	Nonane (C_9H_{20})	-	1.16	1.98
4	Decane ($C_{10}H_{22}$)	2.82	1.01	2.02
5	Undecane ($C_{11}H_{24}$)	3.16	0.85	2.11
6	1-Undecene ($C_{11}H_{22}$)	-	0.44	2.55
7	Dodecane ($C_{12}H_{26}$)	4.02	2.26	3.23
8	1-Tridecene ($C_{13}H_{26}$)	2.47	1.03	4.58
9	Tridecane ($C_{13}H_{28}$)	4.36	1.67	4.97
10	1-Tetradecene ($C_{14}H_{28}$)	2.88	-	10.93
11	Tetradecane ($C_{14}H_{30}$)	5.54	6.98	5.46
12	1-Pentadecene ($C_{15}H_{30}$)	5.89	2.87	8.42
13	Pentadecane ($C_{15}H_{32}$)	11.7	15.25	12.26
14	1-Hexadecene ($C_{16}H_{32}$)	2.77	5.08	3.98
15	Hexadecane ($C_{16}H_{34}$)	6.75	8.93	4.86
16	8-Heptadecene ($C_{17}H_{34}$)	6.81	8.69	6.38
17	1-Heptadecene ($C_{17}H_{34}$)	3.14	5.61	2.99
18	Heptadecane ($C_{17}H_{36}$)	14.2	19.2	7.31
19	Undecyl cyclohexane ($C_{17}H_{34}$)	3.14	5.11	-
20	Hexadecanoic acid ($C_{15}H_{31}COOH$)	0.39	-	-
21	Cis-9 octadecenoic acid ($C_{17}H_{33}COOH$)	6.0	-	1.01
22	Cyclopropanenonanoic acid ($C_{11}H_{21}COOH$)	1.57	-	-
23	Pentadecanoic acid ($C_{15}H_{31}COOH$)	-	1.56	-

There are some derivatives of benzene in liquid products, which can be interpreted as of the role of FCC catalyst in reactions. In addition, the possible evidence is the cyclization reaction of the unsaturated hydrocarbon chain such as 1-heptadecene.

By using this temperature in the liquid-phase cracking system, the liquid products are obtained 81.5 % at 400 ^{o}C in comparison with 79.7 % at 370 ^{o}C. C_{15}-C_{19} segments was contained as the large ingredients, which have high cetane number such as n-hexadecane and n-hexadecene of 100 and 91, respectively as green diesel and was obtained about 45.2 % at 370 ^{o}C and 48.8 % at 400 ^{o}C. The main reason is the influence of temperature in cracking reaction. By increasing the temperature between 370-420 °C, hydrogenated triglycerides were degraded into monoglycerides, diglycerides and free fatty acids which were lately transformed into deoxygenated products.

Table 4: Product composition of catalytic cracking reaction at different conditions, 370 ^{o}C, 400 ^{o}C, 420 ^{o}C

Temperature	370 ^{o}C	400 ^{o}C	420 ^{o}C				
Sample	3rd	3rd	1st	2nd	3rd	7th	10th
Water (wt%)	3.9	4.1	6.2	6.0	5.6	5.5	5.4
Unconverted oils (wt%)	6.3	2.5	0.9	1.2	1.0	1.1	1.1
Gas product (wt%)	10	12	13.5	13.4	13.1	13.2	13.0
Free fatty acid number	34	30	17	17	20	23	26

Table 4 introduces the components of the cracking products from 5 samples in a series of 30 experiments being carried out continuously without changing of catalyst at 420 ^{o}C; and the third sample at 370 and 400 ^{o}C conditions. It can be seen that free fatty acid numbers were lower than those at 370 and 400 ^{o}C, which is expected that catalytic activity of regenerated FCC was enhanced and achieved equivalent state after few rounds of experiments (count to the 3rd sample). The presence of higher amount of water (5.6 %) and gas products (13.1 %) at 420^{o}C could be explained by an increase of dehydration and decarboxylation process when temperature was raised up.

The decarboxylation pathway (1) converts the carboxylic acid group in the free fatty acids to straight chain alkanes by releasing CO_2.

$R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CH_3 + CO_2$ (1)

$R\text{-}CH_2\text{-}COOH + H_2 \rightarrow R\text{-}CH_3 + CO + H_2O$ (2)

On the other hand, the presence of H_2 production from cracking reactions might lead to the secondary reaction which is decarbonylation (2) releasing water and CO as by-products. The decarbonylation pathway produces alkanes by reaction of the carboxylic group in the free fatty acids with hydrogen and forming CO and water. The possible mechanisms of formation of products in the experiments were illustrated in figure 5.

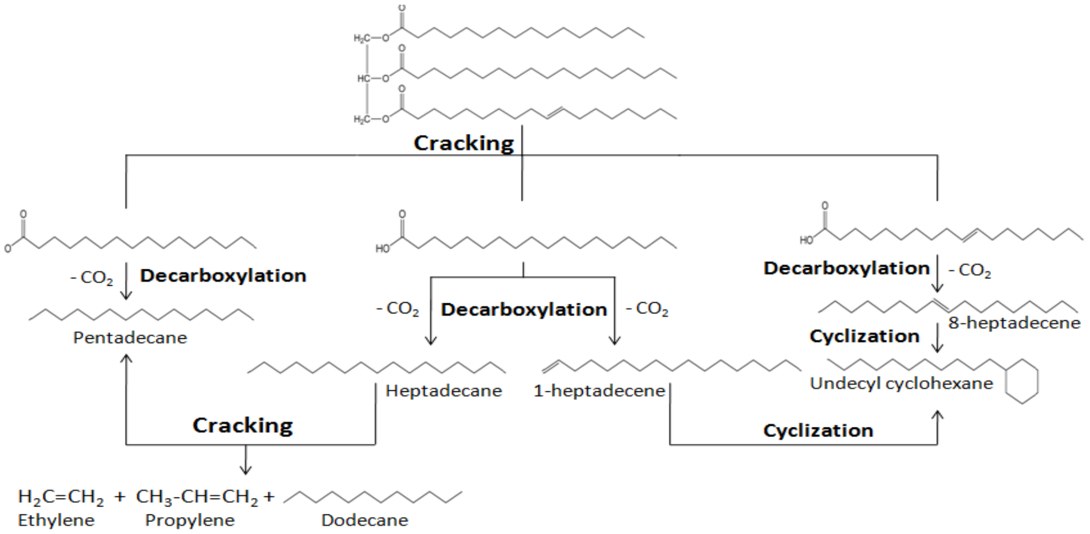

Figure 5: Probable pathways of products formation from catalytic cracking triglycerides in wasted cooking oil

4. CONCLUSIONS

In this research, spent FCC catalyst in Dung Quat refinery was treated by removing contaminated heavy metals. The results of EDX showed that a relatively high amount of Fe, Ni declined after treatment, 56 % and 32 % respectively. In addition, XRD results of regenerated FCC catalyst indicated that the pretreatment did not alter the structure of the original catalyst.

The products in the cracking wasted cooking oil process catalyzed by regenerated FCC were analyzed by GC-MS. Using the liquid phase catalytic cracking, the obtained products are the main of straight chain alkanes from C_{10}-C_{19} and high yield of liquid products, 79.7 % at 370 ^{o}C; 81.5 % at 400 ^{o}C; 80.0 % at 420 ^{o}C in which green diesel accounted for 45.2 %, 48.8 % and 50.8 % respectively. These results support for the advantages of liquid phase cracking process in order to yield higher liquid products as green diesel for fuel. The increasing of temperature may enhance the decarboxylation as well as the dehydration reactions.

The cracking reaction with vegetable oil in different temperature 370 ^{o}C, 400 ^{o}C and 420 ^{o}C indicated that the regenerated FCC catalyst was efficient to achieve an appreciable amount of diesel as well as high quantity of liquid products.

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