

Maja Fabulić Ruszkowski, Marko Radošević, Ivica Jerbić, Jelena Parlov Vuković

ISSN 0350-350X

GOMABN 49, 1, 37-67

Prethodno priopćenje/Preliminary communication

UDK 665.644.2.002.33 : 665.334.94 : 665.347.8 : 665.353.4 : 665.112.2

USE OF BIO-COMPONENTS IN CATALYTIC CRACKING PROCESS

Abstract

Various types of bio-components, such as all types of edible oils (sunflower, rape, palm), used edible oils may be used in the fluid catalytic cracking process as part in standard FCC feed.

In this work, the used sunflower oil was chosen as a feed added to the standard FCC feedstock in the quantity of 10 v/v % and 20 v/v %. Testing of yield and distribution of products (gas components, LPG, FCC gasoline, light cyclic oil, heavy cyclic oils, and coke) has been performed by the micro-activity test and the obtained results have been compared with the yields and products obtained from the standard feedstock. The equilibrium zeolite catalyst from the commercial FCC unit was used.

It was shown how the use of bio-components as the standard FCC feed has been proven to meet the requirements for use of bio-fuels in road transportation, as well as to provide a quality disposal of used edible oils without high added costs.

1. Introduction

The oil price increase and the reduction of its reserves, which also leads to decreased amounts of motor fuel of mineral origin, has intensified the research projects for gaining motor fuels from renewable resources. Today the most significant fuels from renewable resources used in transport are biodiesel and bioethanol.

The Directive 2003/30/EC of the European Union which promotes the use of bio-fuels in road transportation has set its indicative goals for biofuel portions within the total quantity of fuels for 2005 of 2,0 % and for 2010 of 5,75 %¹. It is the vision of the EU for biofuels to cover 20 % of the total fuel market by the year 2020.

On April 19, 2007 the government of the Republic of Croatia decided that fuel distributors have to start with biofuel distribution on the Croatian market in the amount of 0,9 % from the total energy consumption by fuel in 2007².

Most common biofuels are different kinds of bio-components such as all kinds of edible oils (sunflower, rapeseed, palm oils) and waste edible oils.

Although according to the Waste Act, as well as to other acts in the Republic of Croatia, waste edible oil is not defined as hazardous technological waste, it requires constant monitoring and controlled handling. Alike mineral oils, vegetable oils are often inadequately managed.

In the Republic of Croatia only 3 000-4 000 t of waste edible oil is collected (data from 2006) ³, and 7500 t (data from 2007) ⁴, although there 50 000 t of it is sold on the market. To this point only 10 % or 15 % of the total market amount was used. The implementation of regulations on used oils management ⁵ is aiming to establish the system of collecting used oils due to processing or management. Significant increase of collected waste oil is planned up to year 2010 as well as processing of up to 90% of collected waste oils.

1.1 Waste edible oil as bio-component

Waste edible oils, including sunflower oil, are made of triglycerides or in other words chain fatty acids connected in glycerine basis through carboxyl groups. Physical and chemical characteristics of waste edible oils very much depend on fatty acid composition.

The main technical problem when using vegetable oils as liquid fuels are instability, high viscosity and coke deposits in parts of automobile engine during combustion.

So far vegetable oils were mostly transformed in low-temperature catalytic process in liquid phase, which is actually the transesterification with base catalysts and methanols into fatty acid methyl esters (FAME) which are used as biodiesel. High temperature pyrolytic process with solid catalyst is also used in this procedure ⁷.

1.2 Bio-renewable resources and refinery processes

Bio-renewable resources or feedstock can be used as a fuel on their own or as a component in a blended fuel of mineral origin.

There are several appropriate refinery processes in which edible oils and grease can be used in the production of various bio-fuels ^{8,9}. Separating of production from bio-renewable resources increases the costs of their production so the easiest solution would be to incorporate their production into the existing refinery infrastructure during the production and distribution of fuels. In the world today we have a number of profitable refinery plants for the production of biofuels such as biodiesel (FAME), green diesel and green gasoline.

The problem with bio-components in refinery processes is that they are incompatible with typical refinery feeds and products due to their high acidity and high content of alkaline metals. Therefore this feed needs to be treated before entering a refinery process. The procedure of pre-treatment of bio-components requires additional expenses during production.

1.3 FCC process and bio-renewable resources

In fuel production vegetable oils can be used in a FCC process. Different kinds of bio-components such as all kinds of edible oils and waste edible oils can be used for this purpose. The use of vegetable oils on their own in this process is not recommended due to increased total acidity of a new product which causes corrosion in the equipment.

So called green gasoline is a result of the process in which edible oils and grease are used. This feed necessarily requires a pre-treatment in order to remove catalytic poisons such as alkaline metals and other problematic components such as water and solids. Therefore, a bio-component is mostly blended in the standard FCC feed (Figure 1)⁹.

The literature shows that green gasoline can be produced by cracking edible oils and grease in a FCC unit. When using edible oils and grease the yield of gasoline is similar to the one produced after a standard FCC feed. There has been less heavy and usually undesirable product such as light cycle oil (LCO) and heavy cycle oil (HCO), a significant amount of water due to deoxygenation of feed in the FCC unit and CO_x (CO and CO₂). In this way a higher yield of coke is obtained as well as the higher value of research octane number (RON) of gasoline¹⁰.

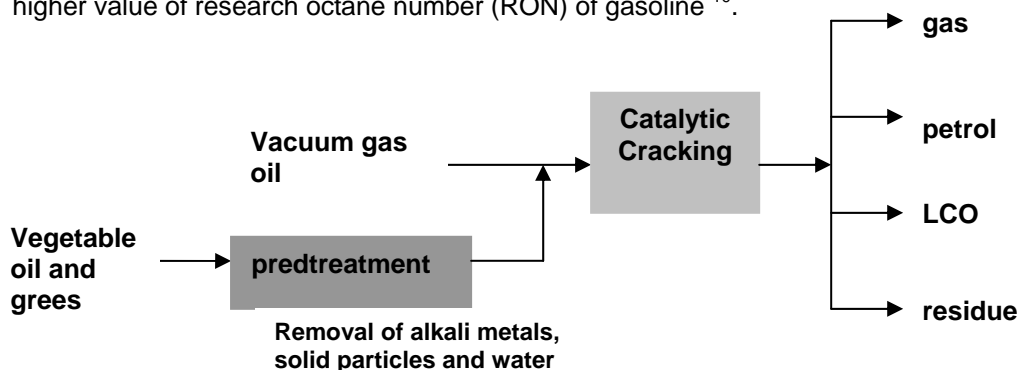


Figure 1: Catalytic cracking process approach of used edible oil and grease

2. Experimental part

2.1 Feeds and catalyst

Standard feed from the Sisak oil refinery with which samples of equilibrium FCC catalyst are tested was used in the experimental part of this paper and this is also a real feed used in the FCC unit in the refinery. Feeds made by blending 10 % v/v and 20 % v/v of used sunflower edible oil in a standard FCC feed (blend 1 and blend 2) were also used. Physical and chemical characteristics of used edible oil and used feeds are shown in Tables 1 and 2.

Table 1: Physical and chemical characteristics of waste edible oil

CHARACTERISTIC	UEO
Density at 15°C, gcm ⁻³	0,9244
Water content, mg/kg	125
Sulphur, mg/kg	4
Chlorine, mg/kg	10
Phosphor, mg/kg	51

The Table 1 shows that waste edible oil was not charged with sulphur or any metals. The NMR spectrum analysis obtained by the NMR spectroscopy did not identify water in the standard feed or blends.

The physical and chemical characteristics change when waste edible oils are added (Table 2).

In the paper a commercial equilibrium FCC catalyst was used which is also the case in the FCC unit in the Sisak oil refinery.

Table 2: Physical and chemical characteristics of feeds

CHARACTERISTIC	STANDARD FCC FEED	BLEND 1	BLEND 2
Density at 15°C, gcm ⁻³	0,8712	0,8762	0,9115
Viscosity (at 100 °C), mm ² s ⁻¹	5,37	6,21	6,11
°API	30,75	29,83	23,59
ASTM 2887 distillation, T, °C, IBP	176,9	195,4	199,5
10 % v/v	334,8	336,3	341,0
30 % v/v	401,7	398,7	403,7
50 % v/v	436,8	432,1	438,6
70 % v/v	468,8	464,3	479,4
90 % v/v	510,2	505,0	512,3
FBP	552,5	554,1	552,0
Sulphur, % m/m	0,9210	0,7848	0,6960
Water, (NMR technique)	-	-	-

2.2 Experiment procedure

Blends 1 and 2 were tested by micro-activity test at reaction temperature of 482, 510, 520, 530 and 540 °C (modified ASTM D 3907 method) and these yields and distributions of products are compared with the yields and product distribution obtained from the standard FCC feedstock. Liquid cracking product was fractionated into petrol and other liquid products (LCO and HCO). Sulphur content, hydrocarbon content and RON were determined for petrol as well as the RON of FCC gasoline by ¹H NMR spectroscopy (method for determining the content of gasoline, 3171-18-03).

Total acidity of feed and liquid cracking product was determined by ASTM D 3242 method. The increase in water content was not noticed.

3. Results and discussion

The paper aims to show that in the FCC process, as an important refinery process, a certain quantity of bio-renewable components (waste edible oils in mineral feed) can be used in a standard gas oil blends as a FCC feed without any significant investments in the infrastructure and all this can contribute to the implementation of a given portion of biofuels in the market.

3.1 Total acidity

Due to increased total acidity of gained cracking product while using bio-components on their own as feeds, corrosion appears on the FCC process equipment. It was recorded that the total acid number of a bio-component can be up to 0,6⁸. For this reason the use of bio-components such as oils on their own is not recommended, but they can come as a certain portion in a standard feed depending on water content and total acidity.

The total acidity of used edible oils, liquid cracking products obtained from a standard FCC feed and liquid cracking products obtained from blends 1 and 2 were determined (Table 3).

Table 3: Total acidity of feeds

Feed/ products	Total acidity, mg KOH/g
Used edible oil (UEO)	1,883
Product from standard FCC feed	0,032
Product from blend 1	0,067
Product from blend 2	0,101

It is shown in the table that the total acidity of used edible oil is very high. The total acidity of products obtained from blend 1 and blend 2 is not high and it does not cause corrosion so it is possible to use 10 % v/v and 20 % v/v of the bio-component in the standard FCC feed without any significant increase of total acidity of products.

3.2 Edible oils cracking and dependence of conversion on temperature

The Figures 2-11 show the dependence of conversion on temperature and distribution and yields of products obtained from the tests. During cracking of vegetable oil their triglycerides are interconnected and through further reactions transformed into fatty acids from which gaseous and liquid hydrocarbons are produced by cracking, aromatization, dealylation and hydrolysis¹⁰.

The Figure 2 shows that temperature increase caused a conversion increase with all the tested feeds. Blend 2 reached the highest conversion and it is followed by blend 2 and a standard feed. It has been recorded in the literature that a feed with higher portion of used edible oil reaches lower conversion when compared to a standard feed due to greater amount of water and CO₂ from carboxyl groups in oils.

3.3 Gas product yield

Temperature increase of cracking reaction with all the feeds resulted in the increase of saturated components of gas. A detailed analysis of gas product obtained by gas chromatography indicates that using of blend 1 and 2 results in increased amount of saturated components of gas C1-C3 (methane, ethane and propane) when compared to a standard FCC feed (Tables 4, 5, 6). A significant increase in propane yield with blend 2 was noticed.

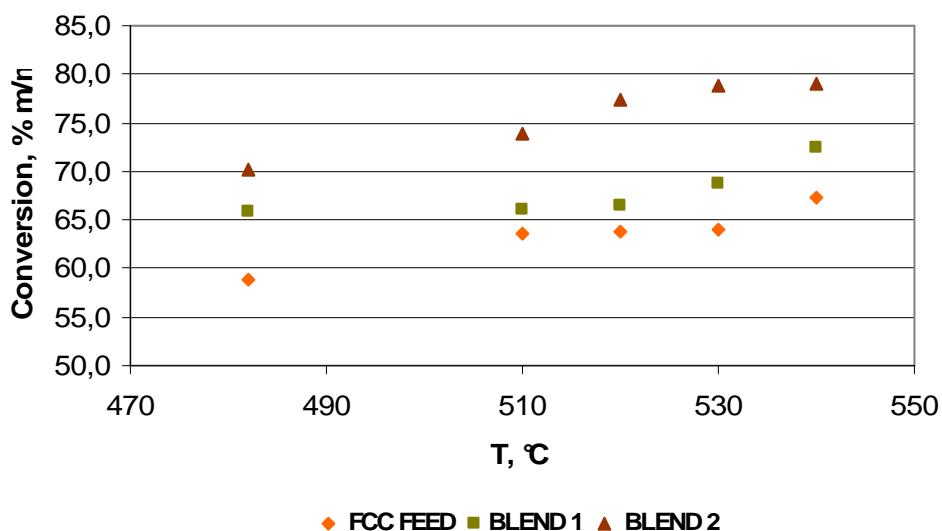


Figure 2: Dependence of conversions on temperature

Table 4: Methane yield in gas

T reaction, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	0,45	0,52	0,61
510	0,66	0,66	0,77
520	0,76	0,73	0,87
530	0,89	0,86	0,99
540	0,97	1,00	1,15

Table 5: Ethane yield in gas

T reaction, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	0,44	0,52	0,57
510	0,56	0,61	0,61
520	0,63	0,67	0,83
530	0,72	0,78	0,90
540	0,81	0,91	1,02

Table 6: Propane yield in gas

T reaction, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	0,98	1,10	1,67
510	1,21	1,20	1,68
520	1,34	1,29	1,77
530	1,48	1,45	1,93
540	1,59	1,63	3,09

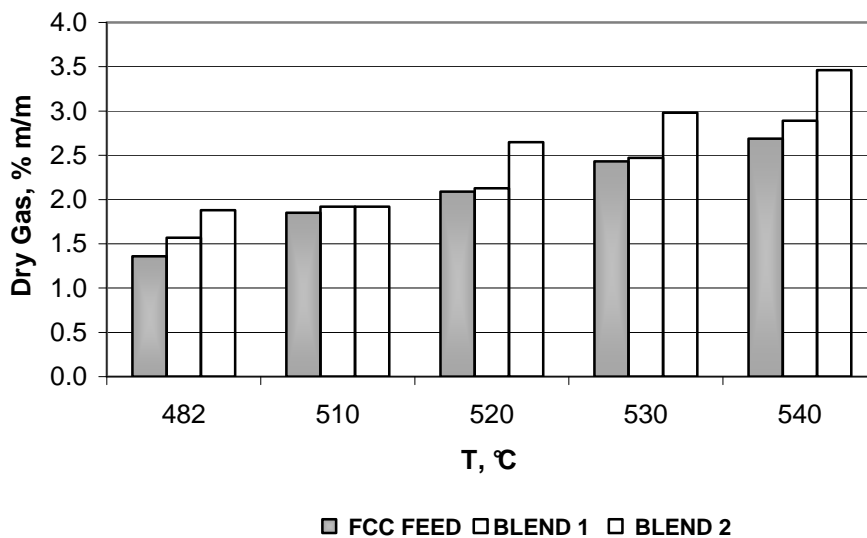


Figure 3: Yield of dry gas at different temperature

The increase of methane and ethane, which along with hydrogen make dry gas, is not desirable in a FCC unit. The amount of dry gas increases with temperature increase in a reactor. The highest increase in dry gas was recorded with blend 2 (Fig. 3).

By using blends 1 and 2 a larger amount of unsaturated C2=, C3= and C4= hydrocarbon components (ethene, propene and total butenes, Tables 7, 8 and 9) has been recorded. Catalytic conversion of fatty acids increases the formation of unsaturated components of gas ¹⁰. The increase of unsaturated C2= to C4= olefins along with the temperature increase is also the result of very endothermic thermal cracking reactions which end up in the increase of breaking C5⁺ aliphatic hydrocarbons C-C bond, as the consequence of which is the increase of newly formed C2= to C4= olefins ¹¹.

Table 7: Yield of ethene at different temperature

T reaction, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	0,48	0,54	0,69
510	0,63	0,66	0,87
520	0,71	0,73	0,96
530	0,81	0,83	1,09
540	0,71	0,98	1,29

Table 8: Yield of propene at different temperature

T reactions, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	2,4	2,74	3,21
510	2,8	2,9	3,75
520	3,03	3,01	3,85
530	3,26	3,37	4,07
540	3,41	3,59	3,96

All the mentioned gases are used as further feeds in petrochemical and oil industry. In the last few years great efforts were done to increase their quantity in refinery processes. Components of liquefied petroleum gas (LPG), isobutenes and butenes with high octane number are especially valuable and are also used in production of oxygenates and alkylates ¹².

The increase of conversion (temperature) with all the used feeds results in the increase of LPG with blends C3 and C4 of hydrocarbons (Fig. 4). The highest yield increase of LPG is reached by using blend 2. Iso-butene from LPG is used with other olefins as a feed for alkylation process.

Table 9: Yield of total butenes at different temperature

T reactions, °C	STANDARD FCC FEED, % m/m	BLEND 1, % m/m	BLEND 2, % m/m
482	6,08	6,48	7,77
510	6,55	6,92	9,64
520	7,21	7,15	10,01
530	7,47	8,62	10,27
540	7,92	9,01	10,43

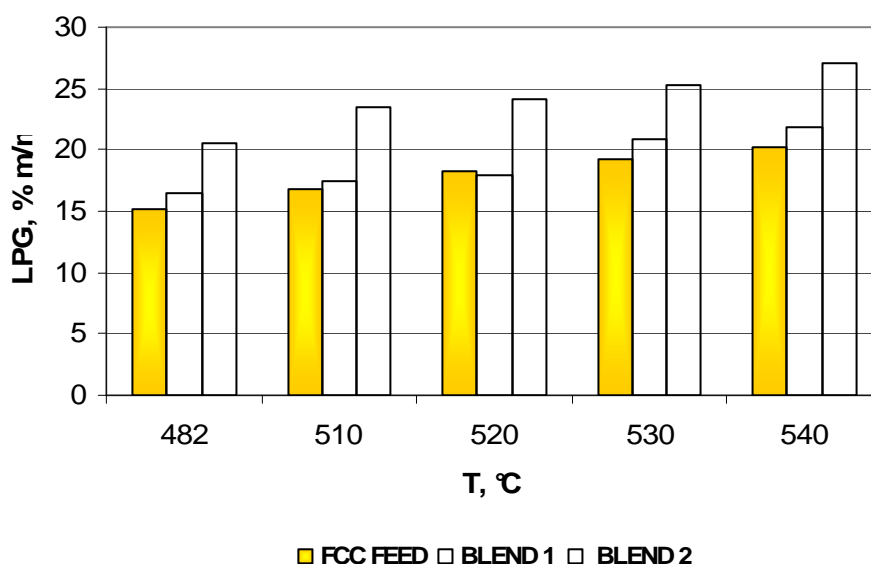


Figure 4: Yield of LPG at different temperature

3.4 Yield of liquid products and coke

In this paper the highest yield of gasoline was obtained by using blend 2 and the lowest yield by using standard FCC feed (Fig. 5). Edible oils are made of long chained hydrocarbon molecules which are broken into shorter chains during catalytic

cracking. A temperature increase results in yield increase of gasoline during cracking reactions increase^{13,14}.

A yield decrease with temperature increase (conversion) was not recorded with standard FCC feed and blend 1 which was noticed with blend 2. When the conversion value is more than 74 % m/m, feed overcracking occurs since there are non-selective reactions of cracking which produce larger amounts of gas, LPG and coke at the expense of petrol yield. Since the aim of process management is the maximalization of petrol yield, special attention has to be paid on the height of conversion in order to avoid overcracking of feed.

The amount of sulphur was determined for the produced FCC gasolines and it has been concluded that waste edible oils did not considerably influence the change of sulphur quantity in the products mentioned. Sulphur quantities in new petrols from blends 1 and 2 were between 800 to 700 mg/kg which matches the decrease of mineral feed portion or the increase of waste edible oil which is almost sulphur-free.

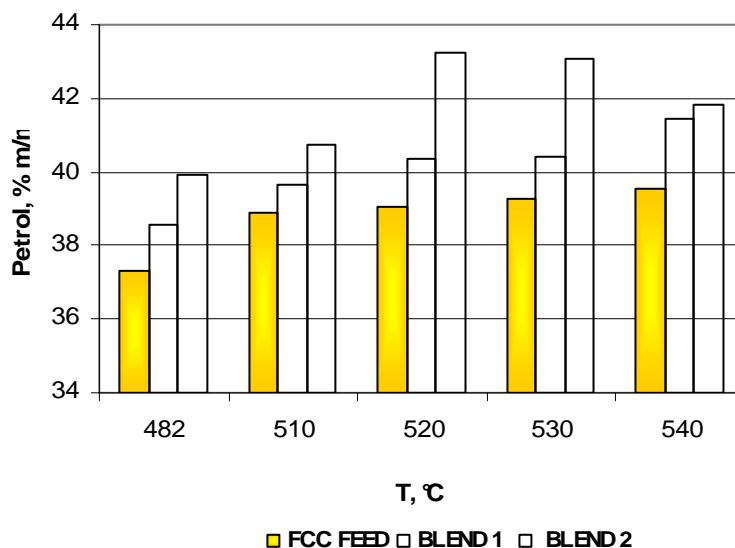


Figure 5: Yield of petrol at different temperature

The FCC unit which tends to produce maximum quantity of products with lower boiling point such are LPG and petrol, light cyclic oil (LCO) and, especially, heavy cyclic oil (HCO) which are considered to be undesirable products of catalytic cracking. Using blend 1 an insignificantly smaller quantity of LCO when compared to a standard FCC feed, while this is more intensified when using blend 2 (Fig. 6).

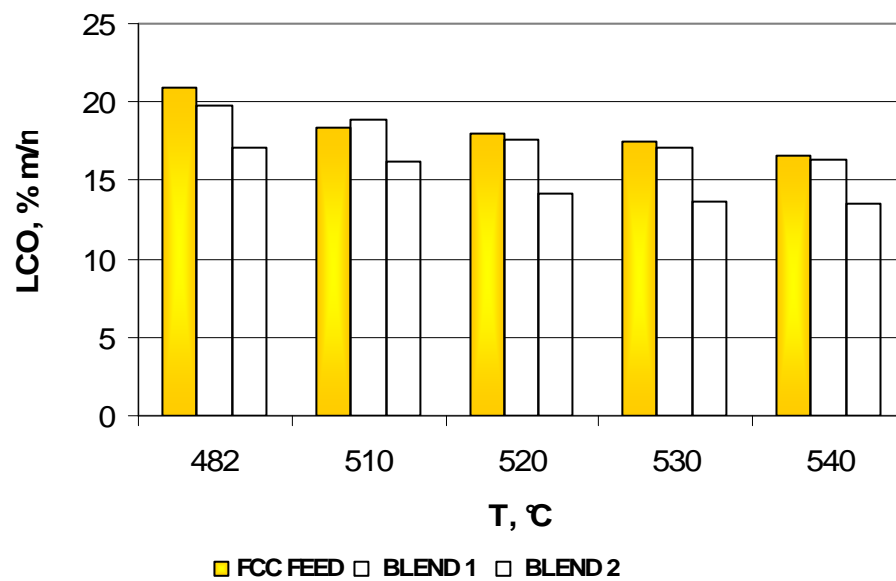


Figure 6: Yield of light cyclic oil (LCO) at different temperature

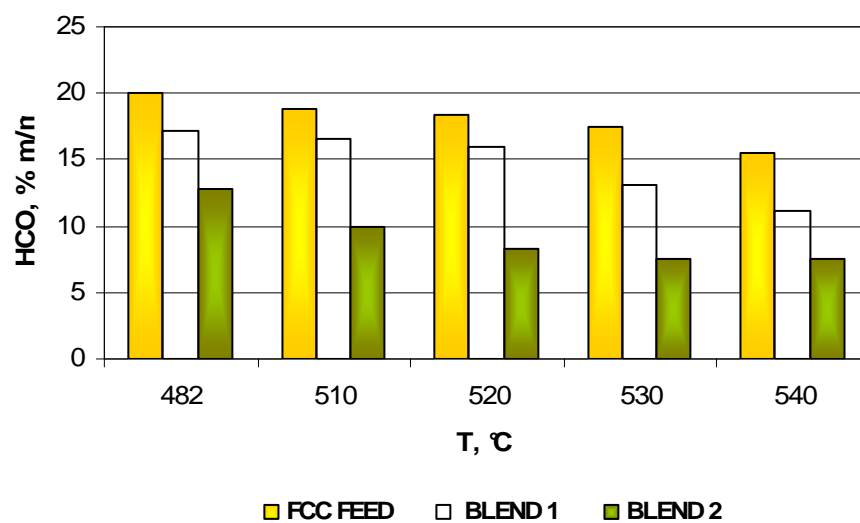


Figure 7: Yield of heavy cyclic oil (HCO) at different temperature

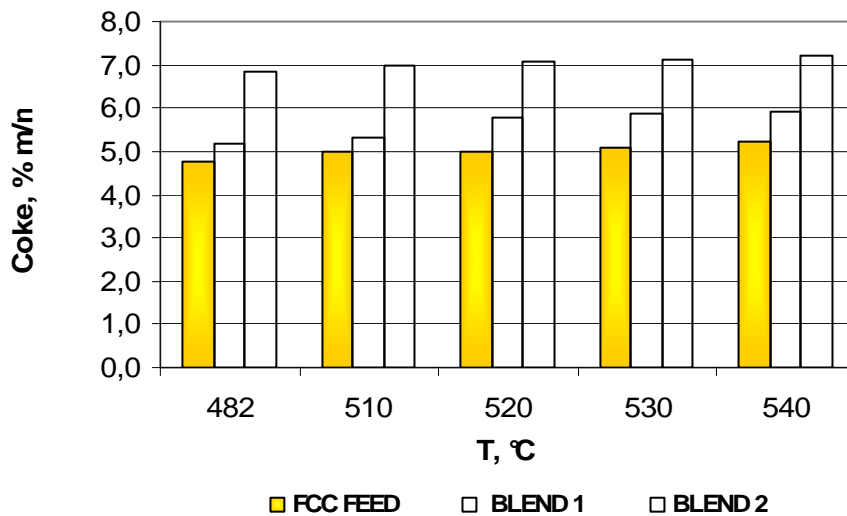


Figure 8: Yield of coke at different temperature

The temperature increase results in reduced yields of LCO and HCO. The highest yield of HCO is reached by the use of a standard FCC feed, it is a bit lower with blend 1, and the lowest yield is with blend 2 (Fig. 7). The obtained results match data from the literature^{8,10}.

Coke is also undesirable product produced during catalytic cracking. During catalytic cracking more coke is produced when using blends, especially blend 2 in comparison with standard feed (Fig. 8). The increased amount of coke is unfavorable since coke tends to create deposits on the surface of a catalyst which reduces its activity. The assumption is that free fatty acids on the surface of a catalyst interact and produce radicals which lead to coke production¹⁰. Coke is also produced by repeated reactions of aromatic dehydrogenation.

3.5 Hydrocarbon content and petrol RON

Increasing cracking temperature causes the increase in quantity of aromatic and olefins in petrol produced from all the feeds (Fig. 9, 10). The quantity of aromatics was between 16,65 and 28,23 % v/v. A significant increase of aromatics was recorded with petrol obtained from blend 2. Aromatic hydrocarbons in petrol are produced by secondary reactions of isomerization, alkylation, cyclization and hydrogen transfer which occur after cracking reactions which include compounds with double bonds or reactions of olefin condensation and other dehydrated kinds^{10, 13, 14, 16}. Repeated reactions of dehydrogenation and hydrogen transfer produce olefins and coke¹⁵. The quantity of olefins was between 10,39 and 20,35 % v/v. The highest

increase of olefins was recorded with standard feeds and the lowest with blend 2. The quantity of produced olefins from edible oil molecules depend on the relation between dehydrogenation and hydrogenation. Olefins are also present in the reactions of condensation when aromatics are produced.

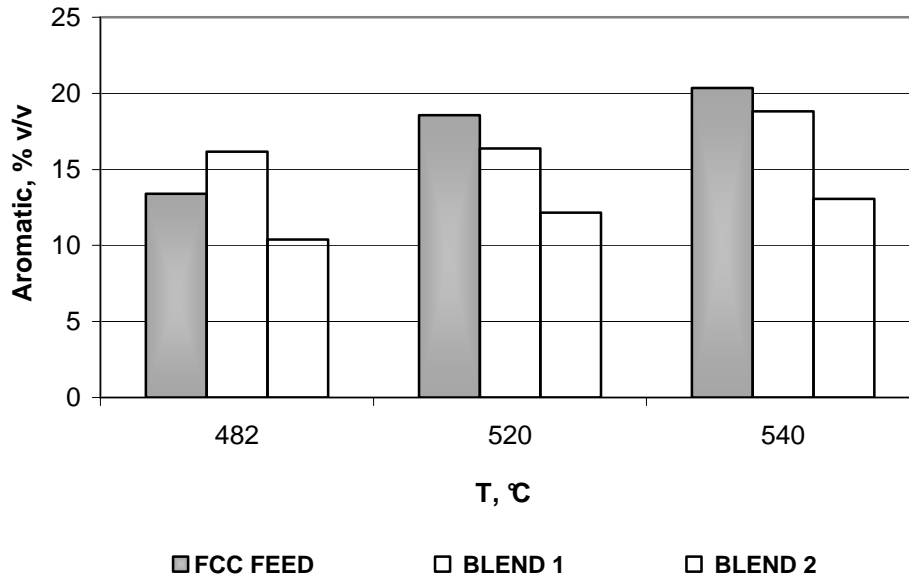


Figure 9: Aromatics in FCC petrol at different temperature

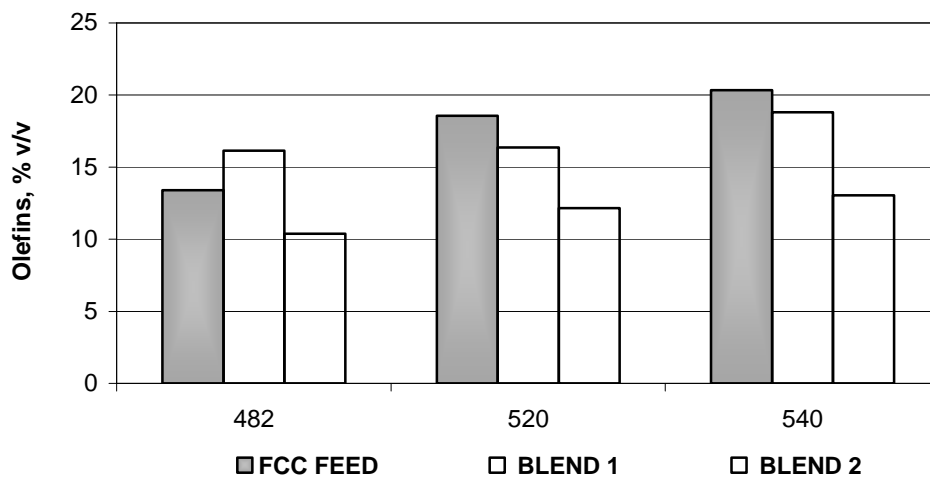


Figure 10: Olefins in FCC petrol at different temperature

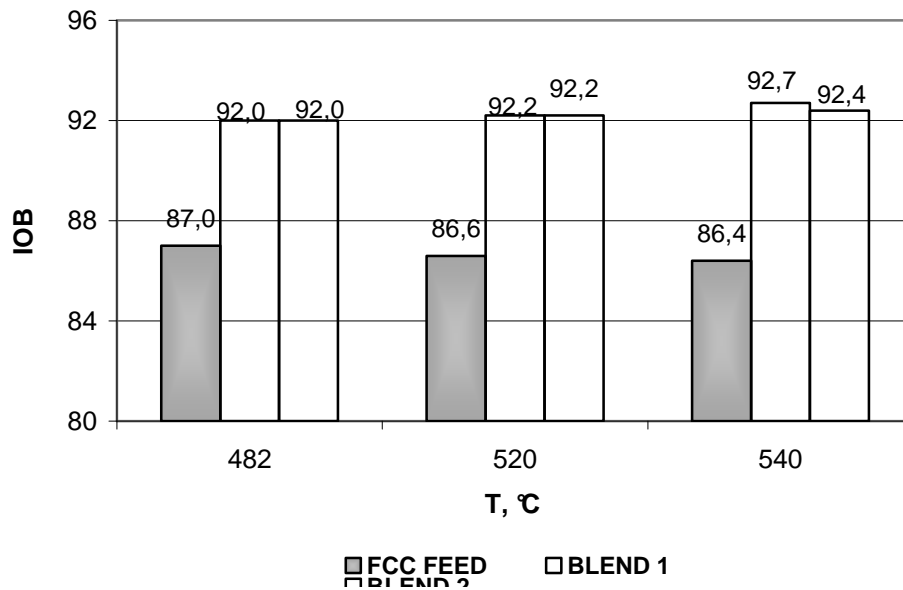


Figure 11: Research octane number in FCC petrol at different temperature

The highest RON was determined in petrol produced from blend 1 with all three tested temperatures, while the lowest RON was recorded with the use of standard FCC feed (Fig. 11).

3.6 Assessment of potential used quantities of UEO in the FCC unit in the Sisak oil refinery

The capacity of the FCC unit in the Sisak oil refinery is 1400 t/d or approximately half a million per year. For blending 5 % of waste edible oil in FCC feed 23800 t/y of WEO is needed, while for blending 10 % of used edible oil in FCC feed 47600 t/y of WEO is needed.

Introducing 0,9 % of biofuel in total energy consumption by fuel in the Republic of Croatia for 2007 matches 22 000 t of biofuels², which makes 16500 t of biofuel when INA's market in Croatia is considered. By blending only 5 % of waste edible oil in FCC feed almost total amount of biofuels in total portion of energy consumption by fuels in the Republic of Croatia, which is the entire amount for the Company, would be met.

4. Conclusion

The following conclusions are derived from the paper:

1. Disposal of waste edible oils needs to be considered from technical and economic aspects, as well as from the aspect of environmental protection.
2. Adding of 10 % v/v and 20 % v/v of waste edible oil in standard FCC feed does not require additional investment costs (except for filtration of waste edible oil), and the products of cracking do not surpass the approved limit of total acidity which would cause corrosion of equipment.
3. Yields and distribution of products produced from the blends were compared to a standard FCC feed. By the use of blends some positive changes have been noticed: with higher yield of gasoline and LPG, lower yield of LCO and HCO, negative higher yield of dry gas and coke.
4. RON of gasoline from blends is higher than RON of gasoline from a standard feed.
5. Waste edible oil is not charged with sulphur and if it was added to a standard feed that would not additionally overdose FCC gasoline and other products with sulphur.
6. Introducing certain amounts of bio-components in the FCC process is a substitute for a part of mineral feed which contributes to introducing biofuels to the Croatian market.

References

1. Directive EU 2003/30/EC
2. Decision on biofuel percentage in total fuel portion in 2007 and biofuel quantity which has to be put on the market in 2007, the Government of the Republic of Croatia (April 19, 2007).
3. www.mzoup.hr
4. Seminar on used oil management (May 20, 2008, Zagreb)
5. Rule book on used oil management, NN 124/06
6. www.azo.hr
7. Vonghia E., Boocock D.G.B., Konar S.K., Leung A., *Energy & Fuels*, **9** (1995) 1090-1096
8. Opportunities for Biorenewables in Oil Refineries, Final Technical Report, UOP, 2005.
9. Holmgren J., Gosling C., Couch K., Kelnes T., Marker T., McCall M., Marinangeli R. *Petroleum Technology Quarterly*, **12** (2007) 4, 119-125
10. Dupain X., Costa D.J., Schaverin C.J., Makkee M., Moulijn J.A., *Applied Catalysis B: Environmental*, **72** (2007) 44-61
11. Katlikaneni S.P.R., Adjaye J.D., Idem R.O., N.N. Bakhshi N.N., *Ind. Eng. Chem. Res.*, **35** (1996) 3332-3346
12. Sadeghbeigi R., FCC Handbook, Gulf Publishing Company, Houston, 2000

13. Charusiri W., Vitidsant T., *Energy & Fuel*, **19** (2005) (1783-1789)
 14. Lappas A.A., D.K. Iatridis D.K., I.A. Vasalos I.A., ERTC 12th, Annual Meeting, Barcelona, 2007.
 15. Corma A., Huber G.W, Sauvanaud L., O'Connor P., *Journal of catalysis*, **247** (1997) 307-327

UDK	ključne riječi	key words
665.644.2.002.33	sirovine za FCC	raw materials for FCC
.002.3	gledište sastava sirovine	raw material constituents viewpoint
.002.33	gledište podobnosti sirovine za obradbu	process capability of feedstock viewpoint
665.334.94	repičino ulje	rapeseed oil
665.347.8	suncokretovo ulje	sunflower oil
665.353.4	palmino ulje	palm oil
665.112.2	otpadno jestivo ulje	waste cooking oil

Authors

Maja Fabulić Ruszkowski¹, e-mail: maja.fabulic-ruszkowski@ina.hr,

Marko Radošević¹, Ivica Jerbić², Jelena Parlov Vuković¹

¹ INA, Technology development and project management department

² INA, Sisak Oil Refinery

Received

February 2nd, 2009

Accepted

January 5th, 2010