

Co-processing of FCC Light Cycle Oil and Waste Animal Fats with Straight Run Gas Oil Fraction

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In the European Union the demand for middle distillates is growing, while a decrease in gasoline demand can be observed. Even the most complex refineries are not able to produce the economic yield distribution from the processed crude oil which constantly meets the changing market demand. The growing need for gasoil can be more and more exclusively satisfied by using unconventional feedstocks, such as bio-originated resources and less valuable refinery streams.

The possibilities of quality upgrade of mixtures containing straight run gasoil, light cycle oil and waste animal grease in different ratios were examined during the series of experiments. The effects of the main reaction conditions (temperature: 300 - 380 °C, pressure: 40 - 70 bar, liquid hourly space velocity (LHSV): 0.75 - 3.0 h⁻¹ H₂/feed ratio: 600 Nm³/m³) on the quality and quantity of products were studied. A favourable reaction parameter combination was chosen to reach the total conversion of triglycerides into alkanes, the saturation of significant part of the aromatic compounds and the desulphurization of straight run gas oil took place. The high cetane number of alkanes, produced during the conversion of triglycerides, compensate the low cetane number of products from the saturation of aromatic components.

1. Introduction

The dependence on import crude (BP, 2013), the growing priority of environmentally sound viewpoints and the limited yield structure flexibility of refineries have been the main driving forces of alternative fuel research and development. One of the major sources of fuel bio-blending components consists of agricultural products (Shell, 2012). In the European Union one of the biggest challenges is to provide gas oil in desired quality and quantity. In an average refinery there can be a lot of low value streams of gas oil boiling range that need quality upgrade e.g. the light cycle oil (LCO) of the Fluid Catalytic Cracker (FCC) plant (Azizi et al., 2013). The sufficient bio component content of modern Diesel gas oils is also important. Its value is defined in the relevant EU directive (European Parliament and Council, 2009). Especially those feedstock mixtures are reasonable to examine which contain the kind of compounds mentioned above.

1.1 Biodiesel

Biodiesel (FAME) is a mixture of fatty-acid-methyl-esters of gas oil boiling range which is produced through transesterification of natural triglycerides. In Europe this is still the most widespread bio fuel producing technology (Shell, 2012), however, the disadvantages of biodiesel (listed below) results in, that it is not too favourable as gas oil blending component. Moreover the construction of the plant necessary for biodiesel production is a greenfield investment, so it can be an economically less favourable project, and that is still not a complete solution for the import crude dependence as the ratio of biodiesel is limited to 7 V/V% in the valid standard.

Main disadvantages of biodiesels (Knothe, 2010):

- Less specific energy content, thus more fuel is used
- Higher cold filter plugging point (cold starting and carburation problems),
- greater portion of double bonds (low heat and oxidant resistance, resin formation),
- high hydrolysis sensitivity of ester bonds (corrosion),

- phosphorous, alkali- and alkali earth metal content, etc.

1.2 Bio gas oil

Bio gas oil (FAME) is a mixture of normal- and iso-alkanes of gas oil boiling range produced by catalytic hydrogenation of triglycerides (Figure 1) and is considered to be a promising gasoil blending component. Furthermore, according to EU regulations bio gas oil produced from waste is to be taken into account twice when calculating the bio component ratio to the total fuel (Baladincz et al., 2012).

As for this product (Table 1), only bad cold flow properties caused by normal alkanes can be mentioned among other disadvantages of biodiesel listed above. However this can be eliminated by further appropriate processing, isomerisation or with the use of additives (Hancsók et al., 2012).

2. Experimental

The purpose of this research was to study the different ways of gas oil blending component production from alternative sources like low value refinery stream and bio derived feedstock mixtures. In accordance with these, experiments were carried out using straight run gasoil containing LCO and waste animal grease in different portions to study the possibilities of heterogeneous catalytic conversion on sulphided NiMo/Al₂O₃ catalyst. The effects of feed composition (waste grease: 0 - 20 %, light cycle oil: 0-10 %) and process parameters on the quality and quantity of the product was investigated.

2.1 Equipment

The experiments were carried out in a 100 cm³ tubular reactor which contained the whole apparatus and all the process units that can be found in an industrial scale hydrogenation plant (Hancsók, 2012).

2.2 Raw materials

The compounds of the feed mixture of heterogeneous catalytic hydrogenation experiments were:

- waste grease from protein processing plant - PPWG (Table 1)
- straight run gasoil from Russian crude oil- SRGO (Table 2)
- light cycle oil from fluid catalytic cracking plant - LCO (Table 2)

2.3 Process parameters

The experiments were carried out under chosen process parameters based on results of previous tests on fatty acid glycerol esters: T = 300-380 °C, P = 40-70 bar, LHSV: 0.75 - 1.0 - 1.5 - 2.0 - 3.0 h⁻¹, H₂/feed volume ratio: 600 Nm³/m³. H₂/feed ratio was defined considering the amount of hydrogen necessary for heteroatom removal and saturating reactions with the use of excess hydrogen.

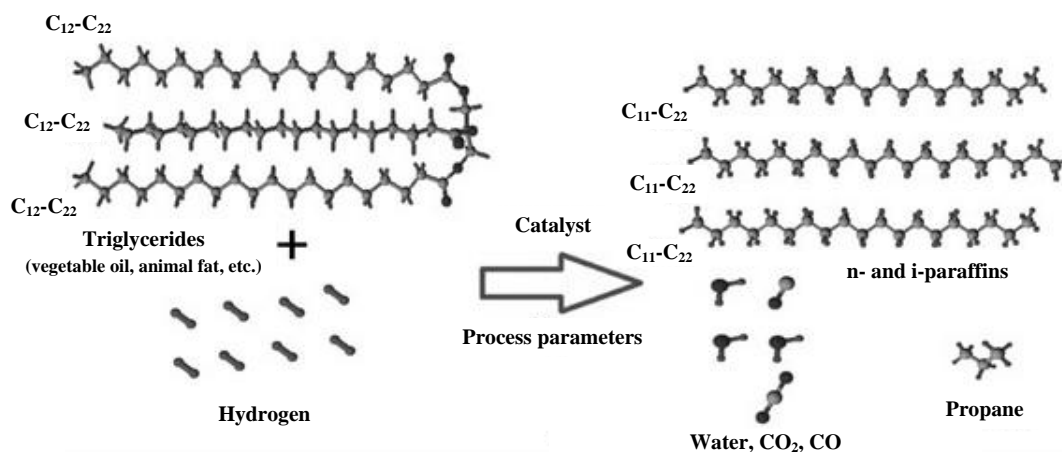


Figure 1: Gross reaction of bio gas oil production (carbon number of the chain depends on the type of the feed) 3 main reaction pathways: decarboxylation ($cn_{\text{paraffin}} = cn_{\text{feed}} - 1$), decarbonylation ($cn_{\text{paraffin}} = cn_{\text{feed}} - 1$) and hydrodeoxygenation ($cn_{\text{of feed}} = cn_{\text{paraffin}}$) * cn =carbon number

Table 1: The properties of waste grease used in the feed

Density at 50 °C	[g/cm ³]	0.8838	Fatty acid composition*	%
Acid number	[mgKOH/100 g]	85	C14:0	2.11
Water content	[mg/kg]	5629	C16:0	23.37
Metal content	[mg/kg]		C16:1	2.82
Ca		195.9	C18:0	16.31
Mg		29.3	C18:1	40.24
K		61.1	C18:2	7.48
Na		70	C18:3	
P		163.6	C22:1	7.63

Table 2: The properties of SRGO and LCO used in the feed

Properties		SRGO	LCO
Density, 15°C	[g/cm ³]	0.8363	0.9583
Kinematic viscosity, 40°C	[mm ² /s]	2.621	2.738
Sulphur content		0.719 %	220 mg/kg
Nitrogen content		23 mg/L	286 mg/kg
CFPP	[°C]		
Monoaromatics	%	18.2	21.76
Polyaromatics	%	8.99	65.35
Total aromatics	%	27.19	87.11

2.4 Analytic methods

The properties of the feed and products were examined by the standardized analytical methods listed in Table 3 below.

2.5 Results and discussion

In Figure 2 and 3 the change of product yield (water, gas, light (C₅-C₁₀), gasoil (C₁₁-C₂₂)) can be observed with the process parameters: LHSV: 1.0 h⁻¹, pressure: 40 and 70 bar, growing grease ratio and temperature from left to right. The greater the grease ratio of the feed is, the lower gas oil yield is achieved. The growth of gas yield is caused by the additional propane generated through the higher conversion of waste grease while water is the product of decarbonylation and hydrodeoxygenation.

Gas oil yield increased when increasing the temperature until 340 °C, above that value it became lower and lower in the applied temperature interval. This was caused by the increasing rate of hydrocracking reactions besides hydrogenation and ring opening reactions. This tendency can be seen in figure 4.

The gas oil content of the product decreased by the increasing of temperature (Figure 5) until 340 °C in case of all feed compositions. The thermodynamic inhibition of aromatic saturation above that temperature results an increasing amount of aromatic content in the product. Increasing the aromatic-free grease content of the feed obviously less aromatic compounds can be observed in the product.

Table 3: Standardized analytical methods for determining product property

Properties	Standard code
Density	EN 12185:1998
Sulphur and nitrogen content	EN 20846:2004
Aromatic content	EN 12916:2000
Distillation properties	EN 3405:2000
Gas chromatography	Shimadzu GC 2010
Kinematic viscosity	EN ISO 3104:1996
CFPP	EN 116:1999

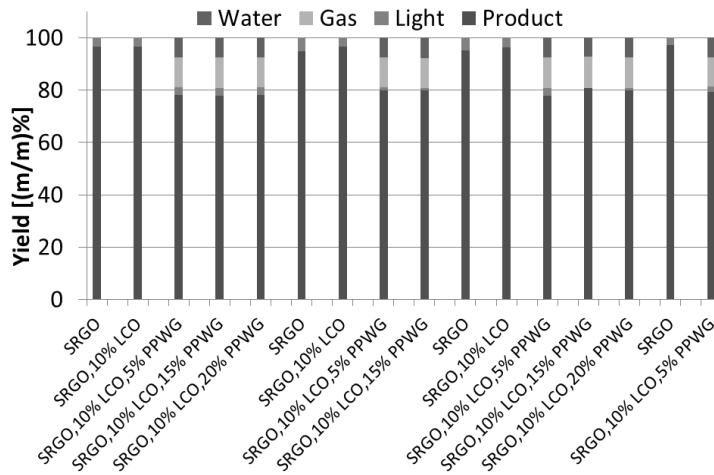


Figure 2: Product yield (40 bar, grease content is increasing from left to right)

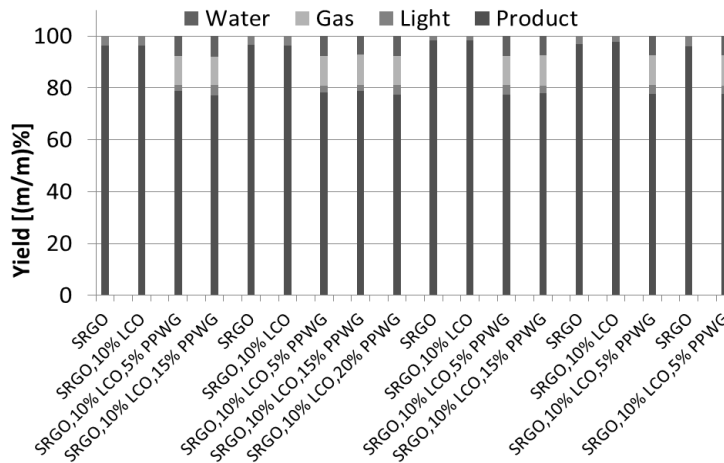


Figure 3: Product yield (70 bar, grease content is increasing from left to right)

Feed composition significantly determines the density of the products. As it is shown in figure 6, LCO ratio results a growth in product density which is definitely compensated by adding more grease to the feed. Figure 7 illustrates the dependence of liquid product viscosity from feed composition and reaction temperature. This property was not influenced by temperature or feed composition and all values fulfil the required values of the relevant EU standards.

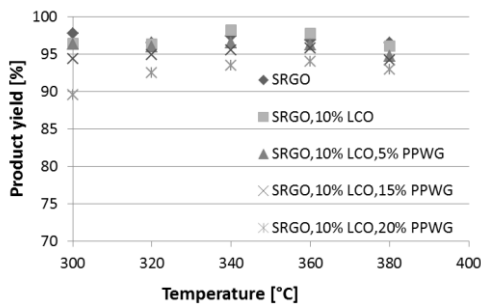


Figure 4: Main product yield as a function of reaction temperature

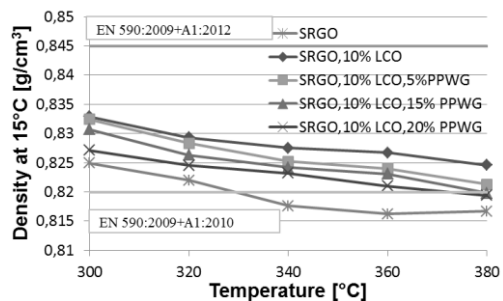


Figure 5: Product density as a function of reaction temperature

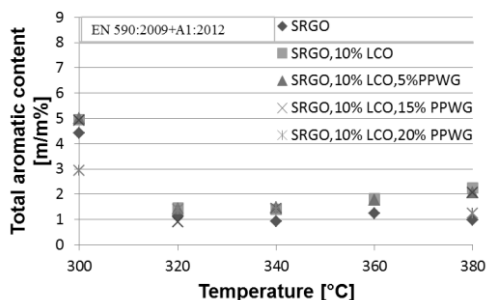


Figure 6: Total aromatic content of products

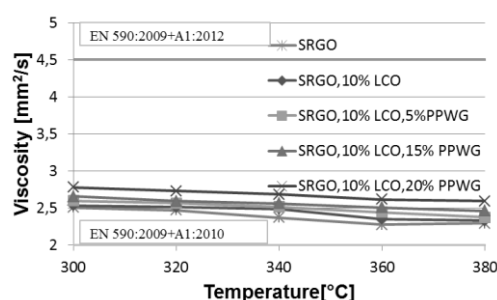


Figure 7: Product viscosity as a function of reaction temperature

The CFPP value of the product was strongly influenced by the portion of grease in the feed (mainly resulting normal alkanes having high freezing point), positive correlation was observed. Figure 8 shows, that none of the products satisfy the gas oil standards of temperate climate.

Another important and standardized property is sulphur content, which is decreasing with decreasing reaction temperature, according to Figure 9. In addition, with the less grease content (low sulphur compared to the gas oil part) in the feed, in case of hydrotreating at 300 °C, the lower the sulphur content of the product becomes, partially due to the originally lower sulphur content in the feed, partially because of the relatively low rate of oxygen removing reactions of the grease and thus the probability of sulphur containing compound conversion is greater (conditions are more favourable for reaching active sites on the catalyst). This tendency is not valid above 320 °C, as competitive oxygen removal reactions accelerate in that temperature interval. The sulphur content of product is satisfactory at and above 320 °C considering the value of the relevant standard (10 mg/kg).

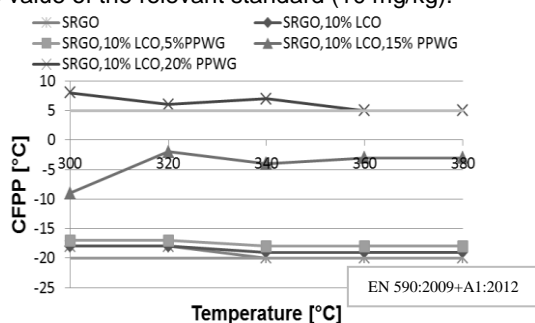


Figure 8: Product CFPP as a function of reaction temperature ($P=40$ bar $LHSV=1.0$ h⁻¹)

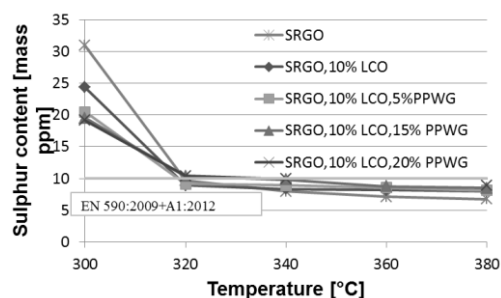


Figure 9: Product sulphur content as a function of reaction temperature ($P=40$ bar, $LHSV: 1.0$ h⁻¹)

Conclusion

In the European Union, providing fuel in appropriate quality and sufficient quantity is a huge challenge especially in the case of gas oil. In an average refinery low quality of gas oil boiling range streams, which are produced in significant quantity such as the LCO of the FCC plant, need further upgrade. In case of modern gas oils the bio component content is also important, so our aim has been to study the possibilities of catalytic quality upgrade of feeds consisting of these compounds. The conversion of straight run gasoil incorporated with LCO and waste grease in different proportions was examined under heterogeneous catalytic hydrotreating conditions on sulphidised NiMo/Al₂O₃ catalyst.

We studied the effects of process parameters (temperature, pressure, LHSV, H₂/feed ratio) on product properties. The most favourable feed composition (75 % SRGO, 10 % LCO, 15 % PPWG) and process parameters (temperature: 340 °C, pressure: 70 bar, LHSV: 1.0 h⁻¹, H₂/feed ratio: 600 Nm³/m³) were found resulting high product yield (78.1 %), and good product quality (density: 0.8252 g/cm³, kinematic viscosity: 2.56 mm²/s, CFPP: -4 °C, sulphur content: 4.9 mg/kg product, nitrogen content: 8.7 mg/kg product, polyaromatics: <0,1 m/m%, cetane index: ≥51) complying with the standard except for CFPP for winter. This problem can be eliminated by using isomerization, additives, or appropriate mixture portions. Taking

these results into account the further aim could be to study the pre-treatment/cleaning possibilities of waste grease in details and a larger scale plant.

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