

Production of Jet Fuel from Renewable Source Material

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Recent demands for low aromatic content jet fuels have shown significant increase in the last 20 years. This was generated by the growing of aviation. Furthermore, the quality requirements have become more aggravated for jet fuels. This was generated by the more severe environmental regulations and the increasing demand for performance requirements. Nowadays reduced aromatic hydrocarbon fractions are necessary for the production of jet fuels with good burning properties, which contribute to less harmful material emission.

The aim of our experimental work was to study the catalytic transformability to jet fuel of 70 – 30 % Hungarian crude oil originating from a previously desulphurized kerosene fraction and a coconut oil mixture at different process parameters (temperature, pressure, liquid hourly space velocity, H₂/feedstock volume ratio). We carried out the experiments on a metal/support catalyst (T = 280 - 360 °C, LHSV = 1.0 h⁻¹, P = 30 - 80 bar, H₂/feedstock volume ratio = 600 Nm³/m³).

Based on the experimental results in case of the studied feedstock the yield and the properties of the products were favourable at the following process parameter combinations: temperature 320 – 330 °C, pressure 50 bar, LHSV 1.0 h⁻¹, volume ratio H₂/feedstock volume ratio 600 Nm³/m³. Based on the quality properties of the product mixtures we determined that we successfully produced products with a high yield (approaching theoretical yield >90%), that have a reduced aromatic content, their performance properties are excellent (eg. crystallization point <-46°C) and they contain biocomponents. These are excellent jet fuel blending components, what are compatible with current fuel systems and jet fuel blending components, they damage the environment less.

1. Introduction

After the global economic crisis, demand for jet fuels shows growing. (Figure 1) (IEA, 2013). Furthermore, the quality requirements were more aggravated for the jet fuels. This was generated by the more severe environmental regulations and the increasing quality requirements. Nowadays reduced aromatic hydrocarbon fractions should be used necessarily for the production of jet fuels with good burning properties, too (Eller, 2013).

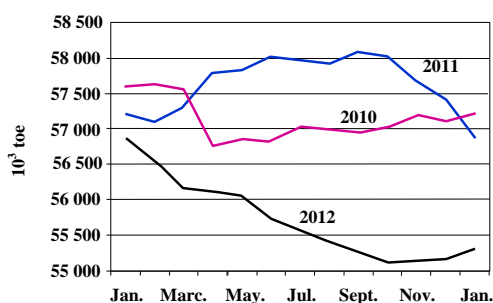


Figure 1.: Demand for jet fuels

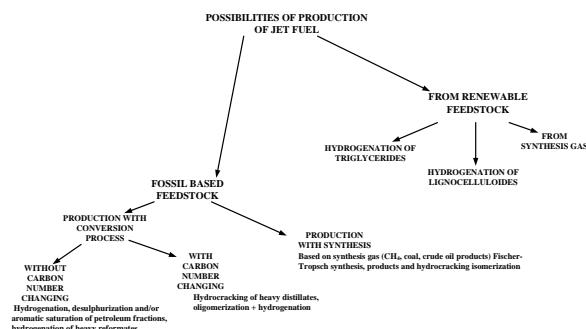


Figure 2.: Classification of jet fuel production possibilities

Present days the jet fuels are produced from different crude oils. By using them environment-friendly (low sulphur and aromatic content) fuels with preferable application technique properties can be produced see Figure 2 (Hancsó, 2011).

During the production of jet fuels efforts must be made to produce high hydrogen/carbon ratio components, so to produce n- and i-paraffins, and cycloparaffins (Blakey, 2011). Isoparaffins have the lowest freezing point; they burn – together with n-paraffins – clean. The cycloparaffins have a lower hydrogen/carbon ratio (Dagaut, 2006), but their energy content raises the energy content of n- and i-paraffins (Hancsó, 2007). Together with isoparaffins, they improve the low temperature properties; this is one of the most important quality properties (Maurice, 2001).

2. Experimental part

According to the previously mentioned, the aim of our experiment was to study the production possibilities of biocomponent containing jet fuels with reduced sulphur and aromatic content (Tóth, 2010). We studied the conversion of 10 % coconut oil containing kerosene fractions. We studied the effects of the process parameters on the yield and quantity of the liquid products.

2.1 Experimental apparatus

The simplified process flow diagram of the apparatus is shown in Figure 3. The effective volume of the reactors was 200 cm³.

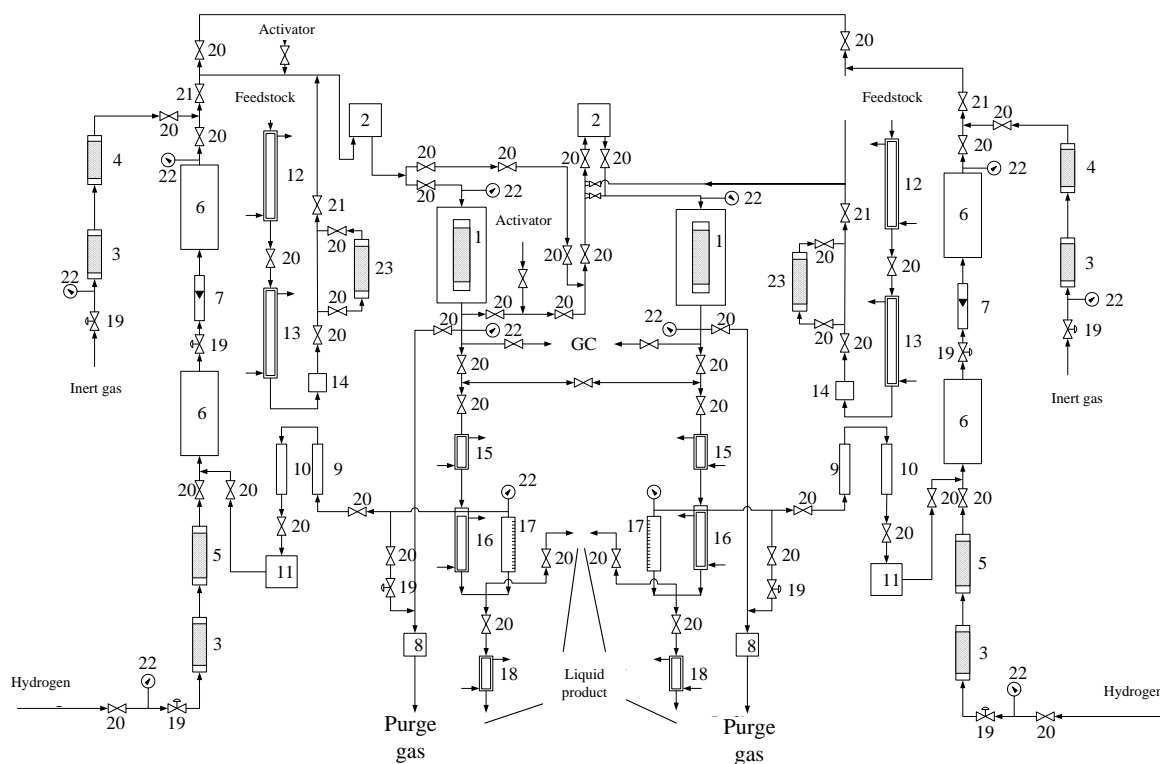


Figure 3: Experimental apparatus

2.2 Materials

We carried out the experiments on an oxide-state Co(2.8%)Mo(11.2%)/Al₂O₃ heteroatom removal catalyst. During our experiments we hydrogenated coconut oil/kerosene mixtures. The applied kerosene fraction was obtained from crude oil with distillation and desulphurization; its parameters are given in Table 1. We used during the triglyceride catalytic conversion experiments Indonesian origin coconut oil as feedstock. We summarized the main quality properties of it in Table 3.

Table 1. Main quality properties of the kerosene fraction

Property	Value
Density on 15°C, g/cm ³	0.8036
Aromatic content, %, (HPLC)	
Monoaromatic	19.9
Diaromatic	0.5
Paraffin distribution, % (GC)	
C10	5.91
C11	18.60
C12	36.45
C13	31.05
C14	7.99
Total sulphur content, mg/kg	4
Crystallization point, °C	-49
Smoke point, mm	26.0

Table 2: Main quality properties of the applied coconut oil

Fatty acid composition, %Coconut oil	
<C8:0	0.63
C8:0	7.73
C10:0	6.08
C11:0	0.03
C12:0	46.98
C13:0	0.04
C14:0	17.9
C14:1	0.07
C16:0	8.86
C18:0	2.88
C18:1	6.86
C18:2n6(c)	1.60
>C18	0.30

2.3 Product separation and test methods

We separated the product mixtures from the coconut oil containing feedstock from the hydrogenation experiments to gas phase, water phase and organic phase (Figure 4.).

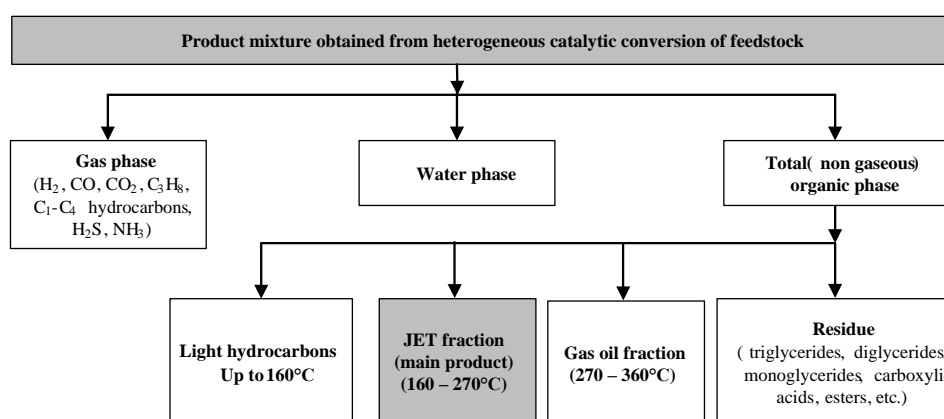


Figure 4: Theoretical scheme of separation of product mixtures produced by hydrogenation of coconut oil containing kerosene fractions with catalytic hydrogenation

The main quality properties of the petroleum fraction and coconut oil, which was used as feedstock and the liquid products of the heterogeneous catalytic experiments were determined according to the standards with the prescribed tolerance given in Table 3.

Table 3.: Standardized and not standardized test methods of feedstocks and liquid

Property	Standard number
Density	EN 12185:1998
Sulphur content	EN 20846:2004
Aromatic content	EN 12916:2000
Smoke point	EN 3014:1993
Crystallization point	EN 2047:2002
Paraffin distribution	Shimadzu GC 2010

3. Results and discussion

During the experiments we changed the temperature between 260 °C and 360 °C, pressure was 20, 50 and 80 bar, while the liquid hourly space velocity was 1.0 h⁻¹ based on pre-experimental results. The H₂/feedstock volume ratio was 600 Nm³/m³, we chose that value so that it should be twice as high as the theoretical value. Figure 5 shows the yield of the total liquid products as a function of the process parameters. We determined that the yield of the liquid products was above 85% in every case. The gas phased part came from the hydrocracking of the kerosene fraction components and the gas products of the oxygen removal reactions of coconut oil.

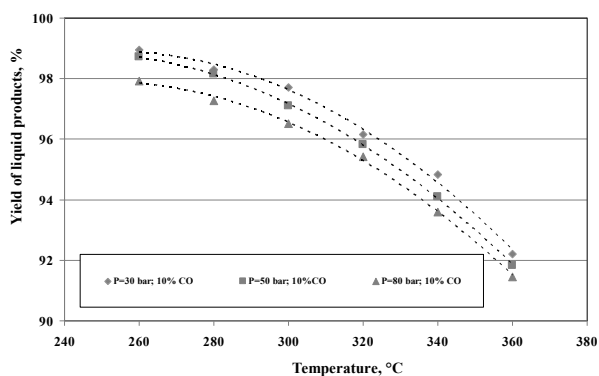


Figure 5. Yield of liquid products as a function of process parameters (LHSV = 1.0 h⁻¹, H₂/feedstock volume ratio: 600 Nm³/m³; CO: coconut oil content)

Figure 6 presents the kerosene fractionated components of the liquid products as a function of the process parameters. With the increasing of the process parameters, the yield of the target product increased, because the conversion of triglycerides was even higher. The shortfall from the theoretical yield value (Table 4.) can be explained with the low grade cracking reactions.

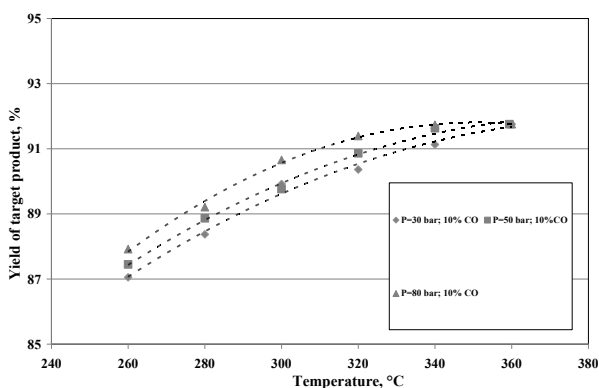


Figure 6: Yield of target product as a function of process parameters (LHSV = 1.0 h⁻¹, H₂/feedstock volume ratio: 600 Nm³/m³; CO: coconut oil content)

Table 4: Theoretical product yields

Triglyceride content of feedstock, %	DCO reactions	HDO reaction
10	96.40	96.77

Figure 7 shows the changing of the aromatic content. Based on the liquid products analyzed with HPLC we determined that the hydrogenation of aromatics took place near the hydrogenation of triglycerides too. The quantity of it was lower than in case of pure kerosene. Basically, the reason is that the triglyceride molecules occupied the active sites of the catalyst from the aromatic compounds. At 360 °C the aromatic content of the products was higher than in case of the products obtained at lower temperatures. The reason is the thermodynamic inhibition caused by the exothermic equilibrium reactions.

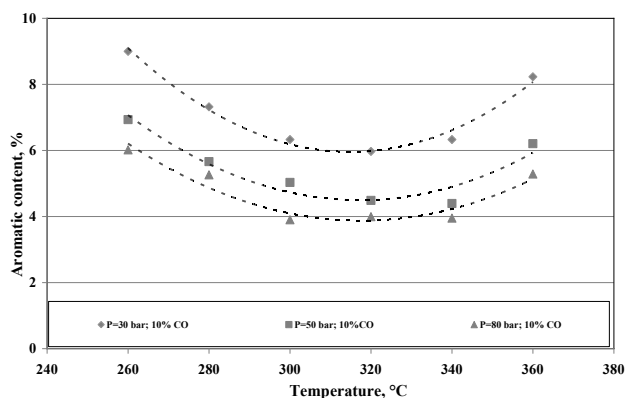


Figure 7: Aromatic content of products as a function of process parameters ($LHSV = 1.0 h^{-1}$, H_2 /feedstock volume ratio: $600 Nm^3/m^3$; CO: coconut oil content)

Figure 8 shows the smoke point of the liquid products obtained with different process parameter combinations increased with the severity of the process parameters. At 280 °C components with favourable combustion properties are in majority. The very high, over 35 mm smoke point values come from the excellent combustion properties of paraffins and cycloparaffins from the hydrogenation of triglycerides and aromatics.

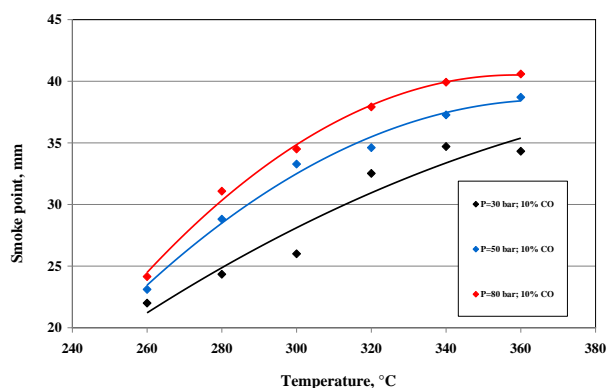


Figure 8: Smoke point of products as a function of process parameters ($LHSV = 1.0 h^{-1}$, H_2 /feedstock volume ratio: $600 Nm^3/m^3$; CO: coconut oil content)

The crystallization point values of the obtained products (Figure 9.) fulfill the standard ($< -47^\circ C$) on and above 320 °C. Crystallization point is affected highly by the n-paraffins formed from triglycerides, which have high freezing points. At the same time, cycloparaffins formed by hydrogenation of aromatics improve the low temperature properties, so the crystallization point decreases a little.

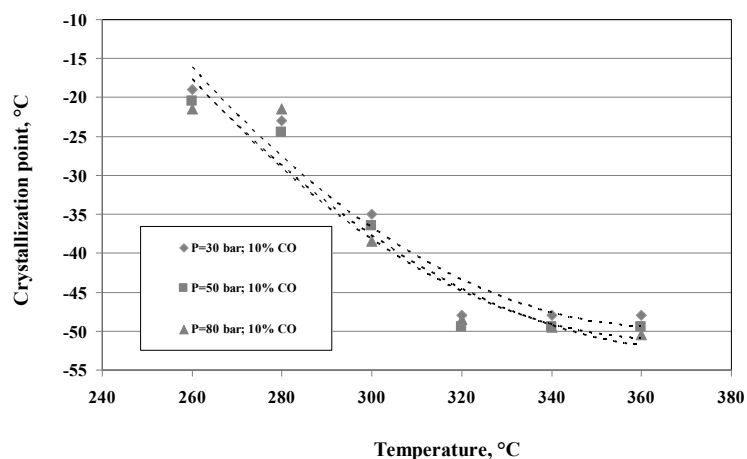


Figure 9: Crystallization point of products as a function of process parameters ($LHSV = 1.0 \text{ h}^{-1}$, $H_2/\text{feedstock volume ratio}: 600 \text{ Nm}^3/\text{m}^3$; CO: coconut oil content)

4. Summary

The aim of our experimental work was to study the possibilities of producing biocomponent containing, reduced sulphur and aromatic content jet fuel. We studied the conversion of different amounts of coconut oil containing kerosene fractions. We carried out the experiments on a great laboratorial heterogeneous catalytic reactor system on a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst. The yield of the liquid products was higher than 85 % in every case, the loss came from the gas products (H_2O , CO_2 , CO , C_3H_8) made by the hydrocracking reactions. We determined that n-paraffins forming from triglycerides improve the combustion properties well, but at the same time they affect crystallization point negatively. After the evaluation we determined the favourable process parameters, which are favourable to produce high paraffin content products: temperature: 320 °C, pressure: 50 bar, liquid hourly space velocity: 1.0 h^{-1} , $\text{H}_2/\text{feedstock ratio}: 600 \text{ Nm}^3/\text{m}^3$.

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