

Biocomponent Containing Jet Fuel Production with Using Coconut Oil

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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 coconut oil 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 - 3.0 h⁻¹, P = 30 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 360°C, pressure 30 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. 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. 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 (Dagaut, 2006).

In aviation by safety aspects the resistance is higher to alternative fuels, compared to the alternative fuels in road transport. This is generated by the extraordinary conditions of aviation - for example very low temperature, great distances with one take-off (Maurice, 2001). Furthermore, alternative fuels must be compatible with the conventional fuels so as not to make problems in the logistics of airports. Of course alternative fuels must be compatible with the actual jet engines and the contacting structural materials too (Blakey, 2011). Present days the jet fuels are produced from different crude oils. For the reason of the growing demand more feedstock sources must be taken into account. By using them environment-friendly (low sulphur and aromatic content) fuels with preferable application technique properties can be produced - Figure 1 (Eller, 2013).

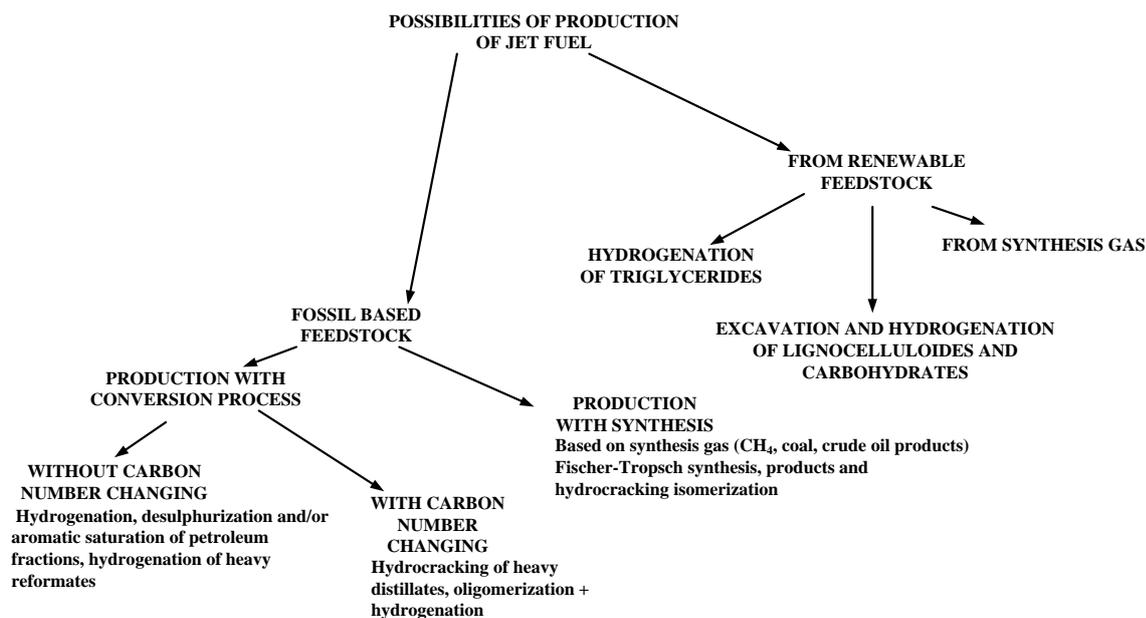


Figure 1: Classification of production possibilities of jet fuels

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 (Hancsó, 2013). Isoparaffins have the lowest freezing point; they burn – together with n-paraffins – clean. The cycloparaffins have a lower hydrogen/carbon ratio, but their energy content raises the energy content of n- and i-paraffins (Lee, 2013). Together with isoparaffins, they improve the low temperature properties; this is one of the most important quality properties (Hancsó, 2007).

2. Experimental

According to the previously mentioned, the aim of our experimental work was to study production possibilities of biocomponent (bioparaffins) what can be blended in to jet fuels. During the experiments we studied conversion of coconut oil with heterogeneous catalytic hydrogenation. We investigated the effects of process parameters to the liquid product yield and quality properties.

2.1 Experimental apparatus

The heterogeneous catalytic hydrogenation experiments were carried out in a reactor system which contained all of the important apparatus and units that can be found in a reactor loop of an industrial hydrogenation plant. The simplified process flow diagram of the apparatus is shown in Figure 2. The effective volume of the reactors was 200 cm³.

2.2 Materials

We carried out the experiments on a presulphided Ni(2.2 %)/Mo(15.2 %)/Al₂O₃ heteroatom remover catalyst. We loaded 80 cm³ catalyst in the middle section of the reactor. We placed Raschig-ring above and under the catalyst bed. To keep the sulphide state of the catalyst we set the sulphur content of coconut oil to 1,000 mg/kg with dimethyl-disulphide.

We used Indonesian commercial coconut oil as feedstock for the catalytic conversion of triglycerides. The main properties and fatty acid composition of this is summarized in Table 1.

2.3 Product separation and test methods

The obtained product from catalytic conversion of coconut oil mixture was separated to gas phase, water phase and organic phase (Figure 3).

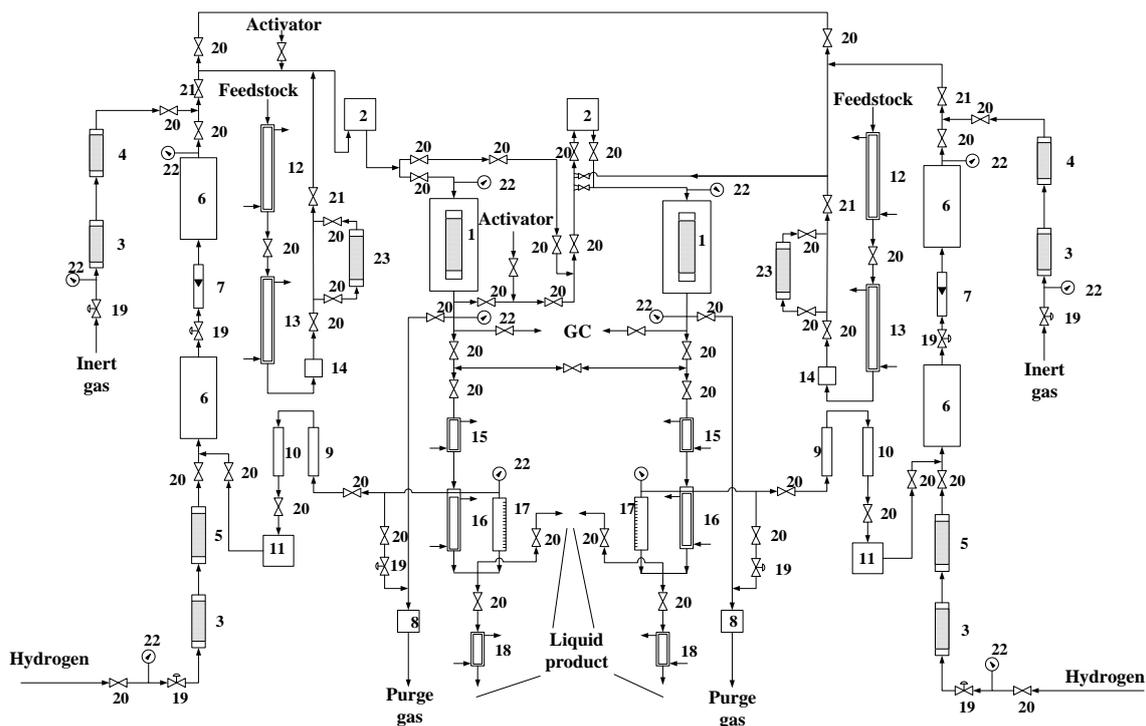


Figure 2. Experimental apparatus (1 reactor; 2 preheater; 3 oxygen transformer; 4, 5 gas dryer; 6, 10 gasfilter; 7 gasflow meter; 8 gasflow meter; 9 dropholder; 11 compressor; 12, 13 feedstock vessel; 14 pump; 15, 18 cooler; 16 separator; 17 level detector; 19 controlling valve; 20 blocking valve; non-return valve; 22 pressure indicator; 23 feedstock dryer)

Table 1. Main quality properties of the applied coconut oil

Quality properties	Coconut oil
Kinematic viscosity, 40 °C, mm ² /s	27.83
Density (15 °C), g/cm ³	0.9231
Fatty acid composition, %	
<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
Water content, mg/kg	648

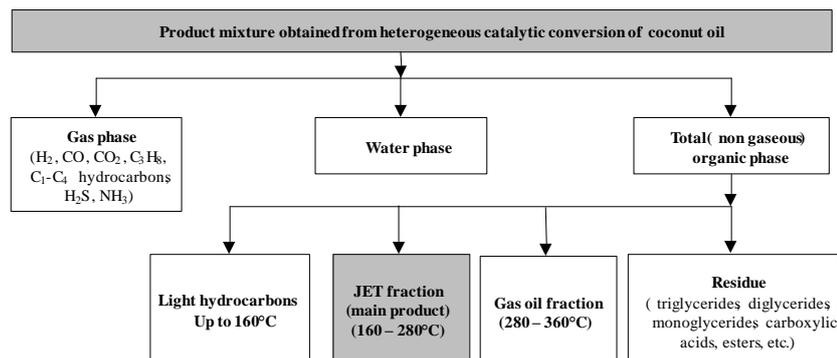


Figure 3: Theoretical scheme of separation of product mixtures produced by hydrogenation of coconut oil containing kerosene fractions with catalytic hydrogenation

We determined the main properties of coconut oil and the products obtained from the heterogeneous catalytic experiments with standardized methods with the given tolerance showed in Table 2.

Table 2: Standardized and not standardized test methods of feedstocks and liquid products

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

We determined the composition of the organic product mixtures from catalytic experiments with high temperature gas chromatographic method (HT-GC), with a HP 6980A and a Shimadzu 2010 GC devices, with application of special, high temperature stable columns.

3. Results with discussion

During the experiments we changed temperature between 260 and 360 °C, the liquid hourly space velocity was changed 1.0 – 3.0 1/h, while the pressure was 30 bar and the H₂/feedstock volume ratio was 600 Nm³/m³ based on preexperimental results. We determined the H₂/feedstock ratio as it must be the more than double of the theoretical decreasing value.

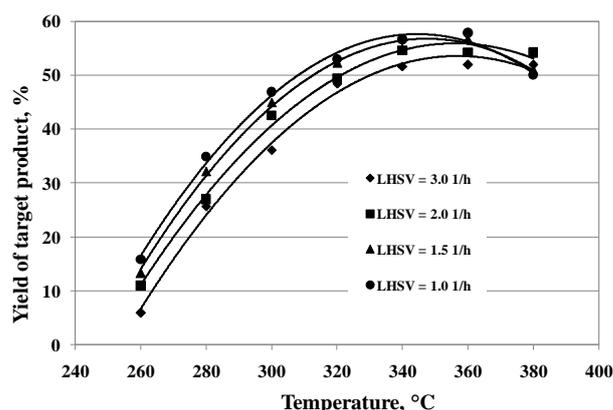


Figure 4: Changing of target product yield as a function of the process parameters ($P= 30$ bar; H₂/feedstock volume ratio: 600 Nm³/m³)

Figure 4 shows the kerosene fraction yield of the liquid products as a function of the process parameters. Aggravating the process parameters (increasing temperature and decreasing liquid hourly space velocity) the yield of target product (kerosene fraction: 160 - 280 °C) increased by the higher conversion of

triglycerides. The loss from the theoretical yields (in case of only HDO reactions take place: 67.67 % (only water is forming during the deoxygenation, paraffins are forming with the same carbon number as the fatty acids of triglycerides); in case of only DCO_x reactions take place: 64.03 %, oxygen removed in form of CO or CO₂, the forming paraffin is shorter with one carbon atom than the fatty acid)) can be explained with the low level cracking reactions.

Increasing the severity of process parameters, the remaining triglyceride content of products decreased well. The residue contained mainly unconverted triglycerides, partially hydrogenated components (mono-, diglycerides, carboxyl acids). Its value was ca. 10 % on 360 °C, and it decreased under 2 % on 380 °C at 1.0 l/h liquid hourly space velocity. The reason is the relatively high oxygen content of coconut oil (14.57 %). The gas oil boiling range side product can be used as an excellent blending component at production of diesel gas oil, because its cetane number is at least 85 - 90 unit (EU standard: min. 51). At the same time, its high CFPP value can be a problem. But, with isomerisation of the n-paraffins it can be decreased under -15 °C.

Sulphur content of the target products decreased well with the increasing of the temperature and the decreasing of the LHSV (Figure 5). (To hold the sulphide state of the catalyst, we set the sulphur content of the coconut oil to 1,000 mg/kg). At the applied lowest temperature the sulphur content was under 100 mg/kg (the actual JET A-1 standard is maximum 3,000 mg/kg), on 340 °C and above the sulphur content of the products was under 10 mg/kg. (This is for the prescription for gasolines and diesel gas oils in the European Union). This is mirroring the high desulphurization activity of the catalyst. It is very important, if we consider the oxygen content of the feedstock, and the removal of sulphur and oxygen carried out at the same site of the catalyst.

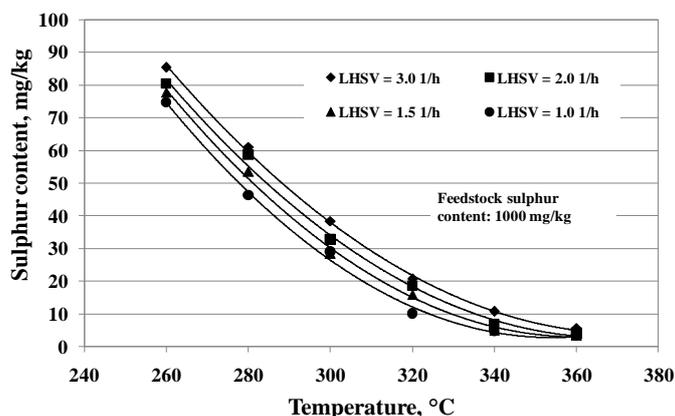


Figure 5: Changing of target product yield as a function of the process parameters ($P= 30$ bar; H_2 /feedstock volume ratio: $600 \text{ Nm}^3/\text{m}^3$)

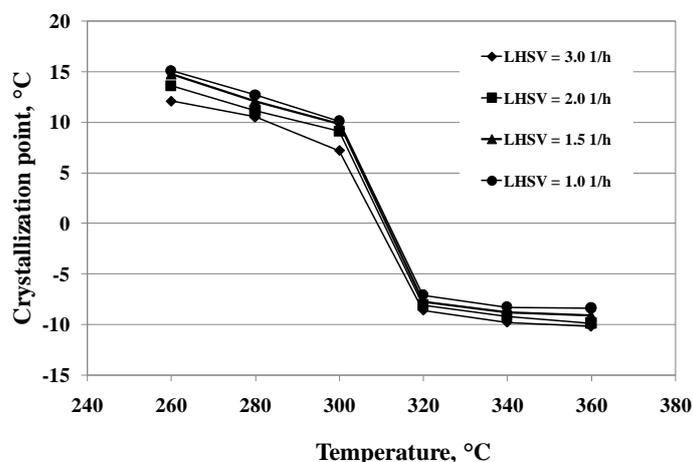


Figure 6. Changing of crystallization point as a function of the process parameters ($P= 30$ bar; H_2 /feedstock volume ratio: $600 \text{ Nm}^3/\text{m}^3$)

The crystallization points of the obtained target product are higher than the standard maximum $-47\text{ }^{\circ}\text{C}$ (Figure 6). The reason is during the hydrogenation n-paraffins are forming from the triglycerides, what have unsuitable. To convert the n-paraffins to isoparaffins there is need to an isomerisation step, after that the product can fulfil the prescription of standard. Above $300\text{ }^{\circ}\text{C}$ we observed a significant decreasing in the crystallization points. The reason is, the freezing point of the forming isoparaffins are much lower than the freezing point of the n-paraffins with the same carbon number.

4. Conclusion

The aim of our experimental work was to investigate production possibilities of biocomponents, what can be used on jet fuels. During this, we studied the catalytic conversion of coconut oil to high hydrogen content paraffin hydrocarbons in the function of process parameters.

We carried out the experiments in a laboratorial heterogeneous catalytic reactor system, on a sulphided NiMo/Al₂O₃ catalyst with process parameters: temperature: $260 - 360\text{ }^{\circ}\text{C}$, pressure: 30 bar, liquid hourly space velocity: $1.0 - 3.0\text{ 1/h}$, H₂/feedstock volume ratio: $600\text{ Nm}^3/\text{m}^3$.

Based on the experimental results, we determined, the yield of the liquid target products approached 60 %, what is higher than 90 % of the theoretical yield. The loss came from the gas products (H₂O, CO₂, CO, C₃H₈) of hydrocracking reactions. The sulphur content of the target products satisfied not just the jet fuel standard (max. 3,000 mg/kg), but above $340\text{ }^{\circ}\text{C}$ and at 2.0 1/h LHSV it was under 10 mg/kg. The formed n-paraffins improved the burning properties (on $340\text{ }^{\circ}\text{C}$ we measured smoke points above 35 mm), but at the same time the affected the crystallization point negatively, the preferable process parameters are the following: temperature: $360\text{ }^{\circ}\text{C}$, pressure: 30 bar, LHSV: 1.0 1/h , H₂/feedstock volume ratio: $600\text{ Nm}^3/\text{m}^3$.

The unconverted residue must be recirculated – after separation – to the beginning of the process for further conversion.

Acknowledgement

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References

- Blakey S., Rye L., Wilson C.W., 2011 Aviation gas turbine alternative fuels: A review, in Proc. Combustion Institute, 2863-2885.
- Dagaut P., Bakali A.E., Ristori A., 2006 The combustion of kerosene: Experimental results and kinetic modelling using 1- to 3-component surrogate model fuels, Fuel, 85, 944–956
- Eller Z., Papp A., Hancsók J., 2013 Production of Jet Fuel from Alternative Source, 9th International Colloquium Fuels, (ISBN-Nr. 98-3-943563-04-7), 543-550.
- Hancsók J., Eller Z., Pölcsmann Gy., Varga Z., 2013, Sustainable Production of Bioparaffins, Chemical Engineering Transactions, 35(2), 1027-1032.
- Hancsók J., Krár M., Magyar Sz., Boda L., Holló A., Kalló D., 2007, Microporous and Mesoporous Materials, 101(1-2), 148-152.
- Lee, E. ,Yun, S., Park, Y.K., Jeong, S.Y., Han, J., Jeon, J.K. 2013, Selective hydroisomerization of n-dodecane over platinum supported on SAPO-11, Journal of Industrial and Engineering Chemistry, DOI: 10106/J.IEC.201306006
- Maurice L.Q., Lander H., Edwards T., Harrison W.E., 2001, Advanced aviation fuels: a look ahead via a historical perspective, Fuel, 80, 747-756