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Fuels from Natural Fatty Acid Esters

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Fuel production from different alternative sources becomes more and more important. One of the sustainable solutions is its production from waste lards (what are proven renewable sources) via different catalytic processes. During our experimental work we studied the catalytic transformation possibilities of (partially) pre-treated waste lard (product from protein plant) and rapeseed oil mixture to fuels. Esterification of fatty acids and following transesterification of triglycerides to fatty acid-methyl-esters (FAME) on acidic ion exchange resin and with K-methylate was studied. The feedstock was converted to i-/n-paraffin mixture with hydrogenation (NiMo/Al_2O_3P) and isomerisation (Pt/SAPO-11/Al_2O_3). The effect of the process parameters on the yield and quality of the products were studied. The obtained product yield approached the theoretical yield – FAME: 85 – 86 %, isoparaffin mixture: 84 – 86 % - in case of 30 % pre-treated waste lard containing rapeseed oil feedstock. The quality properties of the isoparaffin mixture were much better. Besides that, in case of i-/n-paraffin mixture with wide boiling range could be fractionated partially to jet fuel and diesel fuel (satisfying the standards ASTM D-7566-13 and EN 590:2017). These fractions could be excellent blending components of these fuels (adapting product flexibility for market demands).

1. Introduction

The importance of energy and so fuels derived from alternative sources continuously increases word-wide. In the European Union the application of renewable energy sources should be at least 27 % then 35 % until 2030 in every sector (electricity, heat, transport, etc.). In 2030 the legal use of alternative fuels from edible oils will be only 3.8 % according to the winter package of the EU released in 2016 (European Parliament, 2016).

One of the sustainable raw materials of liquid alternative blending components is the natural/waste esters of fatty acids (non-edible ester mixtures: eg. rapeseed oil of high euric acid content; jatropha oil; used cooking oil and fats, waste lards from protein processing plants, glycerides of algaes, etc.). After suitable pretreatment fuels or fuel blending components with different chemical structures can be produced in different catalytical routes from the feedstocks with appropriate fatty acids/fatty acid ester concentration (Srivastava and Hancsók, 2014). For example alkyl-esters of fatty acids with transesterification (mainly with methanol) and following methathesis (Pfister et al., 2017) or hydrocarbon fractions of high isoparaffin content (> 60 %) with hydrogenation and isomerisation of formed n-paraffins in one- (Chen et al., 2013) or two steps (Hancsók et al., 2011) can be produced. Depending on the boiling point range these can be used as blending components of engine gasolines, JET fuels or diesel fuels (Srivastava and Hancsók, 2014). Additionally, many papers discuss on the studies of co-processing of fatty acid esters with unrefined crude oil fractions e.g. by process conditions of Fluid Catalytic Cracking [FCC] (Vonortas et al., 2014) or of hydrotreating [HDT] (Ng SH et al., 2015).

However, relatively few information were presented about catalytic transformation of lards to fuels (Sági et al., 2016). For example, the investigation of catalytic conversion of waste lards to fuel is very important from the aspects of sustainability and low feedstock costs. The main problem of the lard based FAME production is the relatively high amount of impurity and free fatty acid content of waste lards, while only the earlier must be removed in case of hydrogenation.

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2. Experimental

The main target of our research was to study the production of biofuels (a, fatty acid methyl esters; b, i-/n-paraffin mixtures) from vegetable oil containing waste lard (as feedstocks) using different catalytic systems (a, ion exchange resin catalysed esterification of free fatty acids and followed alkali-catalysed transesterification of triglycerides; b, i-/n-paraffin production during heterogenous catalytic hydrogenation and followed isomerisation in one- or two-steps). In this frame our aim was to determine the suitable process conditions (share of waste animal fat in the feedstock and process parameters: temperature, pressure, feedstock/catalyst ratio, etc.). Besides that blending possibilities in different fuels (jet fuel and diesel fuel) of the obtained products were also tested.

2.1 Equipment and experimental methods

The production of fatty acid methyl esters (FAME) was carried out in two steps. The first one was the esterification (over acidic ion exchange resin; 80 – 130 °C; methanol/FFA molar ratio: 2 – 40; LHSV: 0,5 – 2,0 h^{-1}; P: 4 – 8 bar) of the free fatty acids components of the feedstock mixtures. Then it followed the transesterification (in presence of K- methylate; T: 55 °C; methanol/feed molar ratio: 5 – 6:1; P: 3 bar) of tryglycerides of the feed in a pilot scale equipment. This contained an esterification unit with water separator, a vacuum dryer and transesterification reactor, a separator (for glycerin phase) and a FAME aftertreating unit (Srivastava and Hancsók, 2014).

The catalytic hydrogenation/isomerisation experiments were carried out in an high-pressure reactor system containing a tubular down-flow reactor of 100 cm^3. It contained all the equipment and devices (e.g. pumps, separators, heat exchangers, and controllers) which can also be found in the reactor system of an industrial heterogeneous catalytic unit (Hancsók et al., 2007). The hydrogenation experiments were carried out on 80 cm^3 sulfided $NiMo/Al_2O_3$ (Ni: 2.3 %; Mo: 15.1 %; P content: 1.8 %) catalyst (commercially available), followed by the isomerisation of obtained n-paraffin mixtures on Pt(0.5 %)/SAPO-11 (HU 225912 patent) at continuous operation mode.

The catalytic hydrogenation (saturation of olefinic double bonds, splitting of propylene from triglycerides and their hydrogenation, deoxygenation: hydrogenation, decarboxylation, decarbonylation routs) of waste lard containing rapeseed oil feedstocks were investigated on temperature: 280 – 380 °C, pressure: 20 – 80 bar, liquid hourly space velocity: 0.5 – 4.0 h^{-1}, H_2/feedstock volume ratio: 450 – 700 Nm^3/m^3. In order to improve the cold flow properties of the obtained wide cut middle distillate (160 – 360 °C) isomerisation experiments were carried out at temperature: 300 – 380 °C, pressure: 40 bar, liquid hourly space velocity: 0.75 – 4.0 h^{-1}. (Producing of isoparaffins with lower melting point from n-paraffins).

2.2 Feedstocks

The properties of pre-treated waste lard and rapeseed oil are summarized in Table 1. The pretreatment steps of waste lard (from protein processing) were the following: removing the mechanical impurities (filtration); filtration with clarifier and filtration aid materials (≤ 5 μm filter); chemical treatment (citric acid solution); clarification, filtering, washing with water (removal of alkali and alkali earth metals); drying.

Table 1: Properties of pre-treated waste lard and rapeseed oil

Properties	Pre-treated waste lard	Rapeseed oil
Density on 50°C, g/cm^3	0.8985	0.8756
Sulphur content, mg/kg	<10	3.0
Nitrogen content, mg/kg	<10	1.9
Acid number, mg KOH/g	57.5	1.0
Free fatty acid content, %	30.8	0.6
Fatty acid composition (glycerides), %		
C14:0	3.5	0.2
C16:0	30.3	5.8
C16:1	2.3	0.1
C18:0	27.7	2.9
C18:1	23.8	20.9
C18:2	8.4	68.2
C18:3	1.5	0.2
C20:0	1.3	0.8
C20:1	1.2	0.9
C21+	< 0.1	< 0.1
Other impurities (N, P, S, metals), mg/kg	12.5	< 8

2.3 Analytical methods

We used standardized test methods with the given tolerance to determine the properties of each feedstocks and products, EN 14214:2014 (Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods) for fatty acid methyl-esters, EN 590:2017 (Automotive fuels - Diesel - Requirements and test methods) for bio gas oil fractions and ASTM D 7566-13 2017 (JET components from hydroprocessed esters and fatty acids) for jet fuel fractions.

3. Results and discussion

The most important results of many from the esterification experiments carried out with methanol on acidic ion exchange resin will be presented in the following. The tendency of curves on Figure 1 pictures well, that free fatty acid content of products obtained from 10 % pre-treated waste lard (PWL) containing rapeseed oil decreased below 2 % on 110 °C in case of every applied weight hourly space velocity. In case of 50 % PWL rapeseed oil free fatty acid content decreased below 2 % only at 120 – 130 °C. 2 % or less free fatty acid content is important, because these compounds in this concentration do not cause problem during the caustic catalytic transesterification (Knothe et al., 2010). This is supported by the favourable transesterification experimental results obtained using K-methylate. Approaching of the theoretical FAME-yield was higher than > 85 – 86 % (T: 55 – 60 °C, P: 3 bar) as a function of remaining free fatty acid content and process parameters. The approaching of theoretical FAME yield at the transesterification of neat pure rapeseed oil was 90 – 96 % in industrial scale. (In case of our pilot equipment was 94 %).

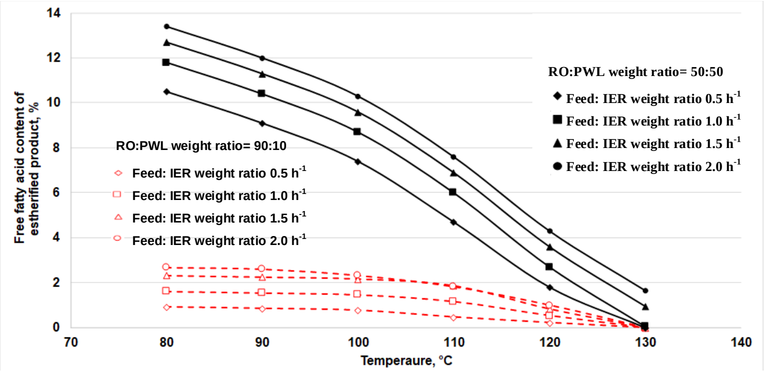

Figure 1: Change of free fatty acids contents of etherified product as function of the temperature [Catalyst: acidic ion exchange resin (IER); FFA content of pre-treated waste lard: 30.8 %; P= 10 bar (inert gas)]

The approach of the theoretical yield was higher than 96 % in case of the obtained bioparaffin products from catalytic hydrogenation of different waste lard containing rapeseed oil mixtures on 340 °C (Figure 2).

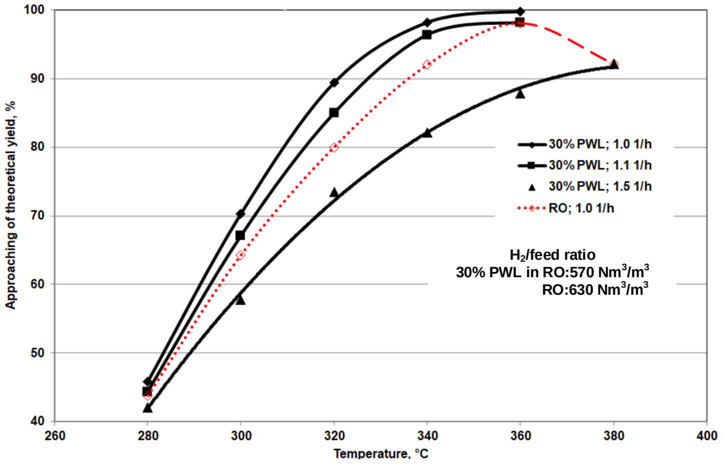

Figure 2: Approaching of theoretical bioparaffin yield as a function of the temperature (PWL: pre-treated waste lard; RO: rapeseed oil)

Results obtained with 30 % PWL feedstock on 1.1 h^{-1} nearly overlaped with results registered at 1.0 h^{-1} in case of rapeseed oil feedstock. This could be explained with the hydrogenation of free fatty acids in the 30 % PWL feedstock which were carried out more faster than the hydrogenation of triglycerides in rapeseed oil (there is no splitting and hydrogenation of propylene to propane). Besides that the large glyceride molecules inhibit the access to the active sites of the catalyst compared to the fatty acid molecules. The capacity of an existing plant could be 10 % higher, if the feedstock (rapeseed oil) contains 30 % PWL.

The favourable process parameter ranges and values based on the summarized evaluation of numerous experimental results from hydrogenation were determined (Table 2). Higher liquid hourly space velocity and lower hydrogen/feedstock volume ratio can be used in case of PWL containing feedstocks what can result significant cost reductions. The reason is the lower hydrogen demand of n-paraffin production from fatty acid content of PWL compared to hydrogen demand of triglycerides (same fatty acid structure assumed).

Table 2: Favourable process parameters (Bioparaffin production)*

Parameters	Feeds	
	5 – 50 % RWL in RO	RO
	values*	
Temperature, °C	330 – 340	340
Pressure, bar	40	40
LHSV, h^{-1}**	1.1 – 1.2	1.0
H_2/feed ratio, Nm^3/m^3	550 – 580	630

**optimized results on many experiment series and long-term experiments (> 400 h)*
***liquid hourly space velocity*

The determined yield of isomerate was higher than 98.5 % on 340 – 360 °C and on 1.0 – 2.0 h^{-1}, while the isoparaffin content was higher than 50 % on 350 – 360 °C and 0.5 – 1.5 h^{-1} (e.g. 64.8 % at 1.5 h^{-1}) based on yield data and isoparaffin content of the obtained products from n-bioparaffin isomerisation experiments and as a function of process parameters (Figure 3 and 4).

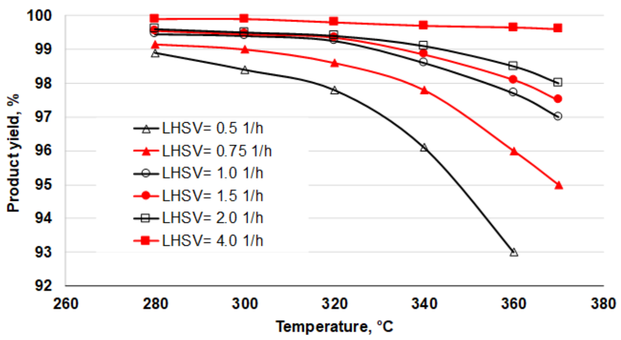

Figure 3: Yields of liquid products of bioparaffin isomerisation as function of the temperature at different LHSV (P = 40 bar, H_2/feed ratio = 400 Nm^3/m^3; PWL/RO feed weight ratio = 30:70)

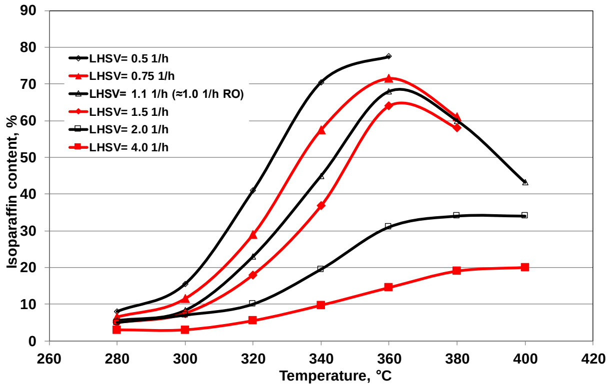

Figure 4: The isoparaffin content of the products as function of the temperature at different LHSV (P = 40 bar, H_2/feed ratio = 400 Nm^3/m^3 PWL/RO feed weight ratio = 30:70)

The main quality properties and yields of products obtained at favourable process parameters from 30 % PWL containing rapeseed oil esterification and transesterification (FAME production), and from hydrogenation and isomerisation are summarized in Table 3. Actual standard values are given too for comparison. Data shows that biodiesel (FAME) could be produced at the same yield as bio gas oil (isomerised bioparaffin mixture) and biojet fuel together; on the other hand the quality of bio gas oil is much better than FAME.

Table 3: Main properties of biodiesel and bio gas oil obtained from PWL (30 %) containing rapeseed oil

Property	Biodiesel*	EN 14214:2014 biodiesel **) (winter grade)	Bio gas oil* (isoparaffin mixture)	EN 590:2017 - Diesel fuel **) (winter grade)	BioJET (isoparaffin mixture)	ASTM D7566-13 (JET standard)
Yield, %	85 - 86	-	70 (260 - 360 °C) - 82 (160 - 360 °C)	-	4 - 14 (160 - 260 °C)	-
Density, kg/m^3	875 - 881	860 - 900	775 - 785	820 - 845	733 - 745	730 - 770
Cetane number	50 - 51	> 51	75 - 90	> 51	-	-
CFPP, °C/ Freezing point,°C	(-4) - (+4)	≤ -20	(-20) - (-25)	< -20	-49	-40
Heating value, MJ/kg	37.5	~38	~44	~43	43.5	-
MJ/dm^3	33.5	~34	~34	~36	33.5	-
Polycyclic Aromatic content, %	0	0	0	≤ 8	0	0
Sulphur content, mg/kg	< 5	< 10	< 1	< 10	< 1	< 1

* Without additives; ** Temperate zone; CFPP: Cold Filter Plugging Point

Based on the detailed evaluation summarizing the advantages and disadvantages of the conversion of pre-treated waste lard to biofuels in case of different catalytic processes are the followings:

Renewable, waste and low-cost feedstock, but must be pre-treated; higher product yield (biodiesel, bio-isoparaffin mixtures: bio gas oil, bioJET) because there is no propane split and only water forms during the esterification (no $–CH_2–$ loss because there is no CO-, CO_2 forming); shorter fatty acid length compounds of lard molecules decreases the product yields.

Risk of soap forming occurs by the presence of free fatty acids during biodiesel production. The soap has emulgeator effect, so the phase separation is difficult. Transesterification velocity by weight is lower because the lower molecular weight triglycerides, so there is need for more catalyst. CFPP values of products are higher due to the higher saturated fatty acid share of the products, while cetane numbers are lower, because the forming FAME contains lower carbon number compounds due to the shorter fatty acid chains.

H_2 demand of biojet/bio gas oil is lower (there is less olefinic double bond content in the molecules of lard). Deoxygenation of FFA is faster compared to the case of triglycerides. Product mixture of isoparaffins has much better performance properties than biodiesel: cetane number is higher with 20 – 30 units, better flow properties; low value refinery streams could be used during the product blending. Fuels composed from C_nH_{2n+2} formula molecules are burning stoichiometric, the pollutant emission is lower.

Product mixtures obtained from hydrogenation allow diesel fuel/jet fuel flexibility suitable for the market demands.

4. Conclusions

Based on the obtained results, waste lard containing (30 %) vegetable oil feedstocks should be suitable pre-treated both for the catalytic esterification and following transesterification, and for the hydrogenation (e.g. deoxygenation) and the following isomerisation to produce good quality product with high yield (mixtures of fatty acid methyl-esters or mixtures of n- and i-paraffins, respectively). With the latter technological solution vegetable oil feedstock of higher waste lard content can be transformed to valuable products than in case of transesterification. The reason is the better feed flexibility of hydrogenation technology caused by the differences existing in the catalytic systems and the reactions to be taken place on them. Yield of fatty-acid-methyl-esters was 94 % of the theoretical yield at the favourable parameters, and its quality satisfied the main requirements of the EN 14214:2014 standard for FAME, except the CFPP (Cold Filter Plugging Point) value which can be improved by suitable additivation. From the waste lard containing vegetable oil feedstock we obtained mixture of n-paraffin hydrocarbons as intermediate product with almost 98.5 % of the theoretical yield on a sulphided $NiMo/P/Al_2O_3$ catalyst at the favourable process parameters (T= 335 °C; P= 40 bar; LHSV= 1.1 m^3/m^3h;

H_2/hydrocarbon ratio 460 Nm^3/m^3). The isomerisation of this n-paraffin product (on an own-developed Pt/SAPO-11 catalyst) resulted 97 % JET- and diesel fuel boiling point range product, and 2.8 % naphtha fraction rich in isoparaffins.

During the processing of the waste lard - vegetable oil mixture the yield of JET fuel is higher comparing to the pure vegetable oil, because waste lard contains free fatty acid esters of lower carbon number, which increases the product flexibility (of a crude oil refinery).

Diesel fuel fraction satisfies the quality requirements of EN 590:2017 standard for diesel fuel with the exception of density and lubricity. The obtained diesel fuel blending components have significantly better performance properties comparing to the product of transesterification. For example, their cetane number is higher in 25 – 30 unit, and CFPP value is lower in 20 – 30 °C. However, their application requires higher amount of lubricity improver additive. To obtain the prescripted 10 % renewable fuel share, in the EU until 2020 it is practical to use together the alkyl-esters and isoparaffin-rich hydrocarbon fractions in a suitable ratio to set the density, lubricity, CFPP value based on compromise.

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