Catalytic cracking of fatty oils and fatty acids – a novel route towards bio-jet fuel

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(Fig. 4, Fig. 5: revised)

Summary

Components for bio-jet fuel production can be achieved by catalytic cracking of fatty oils and fatty acids over activated carbon catalyst. At reaction temperatures of about 450 °C, mainly C15- and C16-n-Alkanes that can be isomerized for jet fuel-usage are produced. They can be used for bio-kerosene after isomerization. Introducing high-oleic feedstock like HO-sunflower-oil and slightly raising the reaction temperature leads to high amounts of n-alkanes in the jet-fuel boiling range. The process proves to be very robust concerning feedstock compositions and impurities. Therefore, catalytic cracking over activated carbon is an ideal pathway to transform not only bio-based oils, but also their wastes and fatty acid-containing by-products from plant oil processing into high-quality fuel components. Using alternative catalysts leads to an enhanced production of alkylated benzenes which are indispensable for aviation jet fuel.

1. Bio-jet-fuel – state of the art

In 2009, the global aviation stakeholders, including the International Air Transport Association IATA, have agreed upon a set of goals to limit aviation's contribution to the global warming, including:

- a carbon-neutral growth from 2020 on, and
- a 50%-reduction of CO_2 emissions by 2050, relative to 2005 levels.

One explicitly stated measure is to improve fuel efficiency (scheduled to reach an average of 1.5% annually to 2020). Improved aviation technology will be one important part of the sustainability strategy – optimizing infrastructure and navigation procedures being the other. But there will be no chance to reach these ambitious goals without partly substituting fossil fuels [1].

While parts of the earthbound traffic can be powered by electricity (railway trains, automotive electromobility), gaseous fuels (Compressed Natural Gas-CNG, Liquefied Petroleum Gas- LPG) or hydrogen (fuel cells), whereas large-scale aviation is restricted to liquid fuels due to their high energy density. Even though there has already been a successful flight of a fuel-cell-powered prototype two-seat Boeing Dimona motor-glider, this concept is discussed for small manned and unmanned air vehicles only. Boeing does not envision fuel cells to power large commercial airplanes [2].

Alternative aviation fuels have to meet strict regulations in order to become certified. In this context, flight safety is a very significant matter. One main issue is that the fuels have to be reliably liquid at -50 °C – a requirement that renders the use of classical "Biodiesel" fuels impossible. These methyl esters solidify already at far higher temperatures. For example, Cold Filter Plugging Point –CFPP – values range from -12 °C for rapeseed oil methyl esters to 9 °C for palm oil methyl esters [3].

Alternative (= not made from crude oil) aviation fuels, made via the Fischer-Tropsch-route, are based upon coal, natural gas and biomass. They are called CtL (Coal to Liquid), GtL (Gas to Liquid) or BtL (Biomass to Liquid). Biomass - being the only sustainable, possibly greenhouse-gas-neutral choice - can be wood, straw, corn, soy, sugarcane or algae [4].

Fischer-Tropsch-derived bio-jet-fuels were the first bio-jet-fuels that were granted an approval by the American Society for Testing and Materials (ASTM). They were followed by Hydroprocessed Esters and Fatty Acids – HEFA –in 2011 [5]. These fuels can be made by hydrotreating of plant oils (preferably palm oil) and their derivates and animal oils and fats. Mainly, they consist of saturated long-chained alkanes, derived from total hydration of the fatty acids. Hence, there must be a further conversion step of isomerization to meet the specifications regarding melting point. The Finnish enterprise Neste Oil aims to launch commercial production of HEFA by the trademark NExBTL. In July 2011, the German airliner Lufthansa started scheduled commercial flights using HEFA and conventional fuel. [6].

Other routes that aim for approval by the ASTM are alcohol-to-jet (ATJ), synthetic kerosene containing aromatics (SKA) and metabolically-derived synthetic kerosene (SKM) [5].

2. Catalytic cracking over activated carbon

Like the HEFA technology, catalytic cracking over activated carbon is a way to convert triglycerides and Free Fatty Acids – FFA – into oxygen-free hydrocarbons. But unlike HEFA production, no external hydrogen is added. The C-atoms of the acid groups break apart from the long-chained part of the fatty acid as well as (in case of triglycerides) from the glycerol backbone. The bound oxygen goes along with the decoupled C-atom, forming CO_2 (decarboxylation) or CO and H_2O (decarbonylation). Simultaneously, a part of the feedstock 'cokes': it turns to substances with an increased C/H-ratio, thereby setting hydrogen atoms free that saturate the terminal remaining C-atom of the formed alkane. To a certain extent, even double bonds of unsaturated fatty acids are saturated. As C16- and C18-fatty acids are the most common ones, the primary liquid products are C15- and C17-alkanes. They have an average cetane number of 100 and therefore form an ideal diesel fuel blend. Secondary liquid products, formed by secondary cracking reactions, cover the kerosene and gasoline boiling range. Fig. 1 outlines the basic process, consisting of evaporation, catalytic reaction and cooling / product separation.

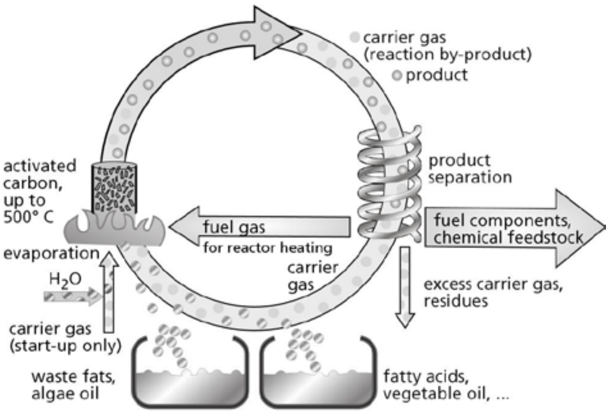

Fig. 1: The process scheme of catalytic cracking

One of the major advantages of the process is its robustness against feedstock compositions and impurities. It works with triglycerides as well as 100 % free fatty acids, water content is only restricted by economic reasons, and non-volatile components remain in the evaporation unit and do not reach the reactor at all.

Therefore, catalytic cracking over activated carbon is an ideal pathway to transform wastes and fatty acid-containing by-products from plant oil processing into high-quality fuel components.

The coking products remain inside the pores of the activated carbon, gradually reducing the pore capacity and finally deactivating the catalyst. To be precise, it could be stated that the process is not a real catalysis because altering the 'catalyst' by coking is part of the process. Obviously, this does not go along with the definition that a catalyst does not change in the process. Activated carbon consumption is about 15 wt.-% of the feedstock; suitable activated carbon catalysts can be recovered after usage by re-activation with steam or CO_2 at up to 1000 °C [7].

The two recently finished projects 'CRACKING' and 'SNG and LPG', funded by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) in the framework of the funding program 'Biomass for energy', investigated the catalytic cracking of bio-based waste fats, plant oil processing by-products and inedible vegetable oils on a lab-scale (60 ml/h feed). Selected experiments in pilot scale (3 kg/h feed) confirm the potential of a scale-up towards industrial applications [7,8].

3. Jet-fuel components by catalytic cracking

3.1 N-alkanes

The primary products of catalytic cracking (C15 – C17) are only slightly more volatile than the primary HEFA products; both of them have to be isomerized in order to fit into the kerosene boiling range.

The process products start to differ from each other when unsaturated fatty acids are introduced. In Hydrogenation, the double bonds are at least partially saturated along with oxygen removal from the acid group [9]. In catalytic cracking, double bonds can be used to selectively lead secondary cracking towards alkanes in the kerosene boiling range.

Oleic acid (*cis*-9-Octadecenoic acid) is one of the most important unsaturated fatty acids. It represents between 35 and 65 % of all fatty acids in rapeseed oil, sesame oil, peanut oil, corn kernel oil, olive oil and goose fat [10]. Special species of safflower and sunflower can produce much higher oleic acid contents, partially of up to 92 % ('High Oleic – HO – oils') [11].

When the temperature is raised above 450 °C or the catalyst contact time is raised above the minimum that is necessary for complete oxygen removal in catalytic cracking, secondary cracking reactions are promoted [8]. Double bonds do not break easy, but the directly or indirectly adjacent single bonds do. Fig. 2 shows the oleic acid molecule with its predetermined breaking points: η for the primary decarboxylation / decarbonylation reaction, α1/2 and β1/2 for the secondary cracking reactions. Furthermore, the C-atoms are numbered.

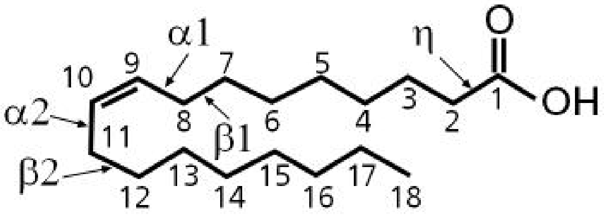

Fig. 2: The oleic acid molecule with predetermined breaking points for catalytic cracking

When C-atom 1 is removed in the primary reaction, secondary cracking at β1 leads to C11 + C6-hydrocarbons, while α2 produces C8 + C9, like shown in Fig. 3. Similarly, breaking at α1 gives C10 + C7, and secondary cracking at β2 leads to C7 + C10. Now, the n-alkanes C6 to C11 fit much better into the kerosene boiling range than the primary C17 (or even the primary C18 HEPA-product) does.

One would expect half of the secondary products to be unsaturated. However, experimental results indicate that these are at least partially saturated internally, just like the terminal C-atom (#2 in Fig. 2).

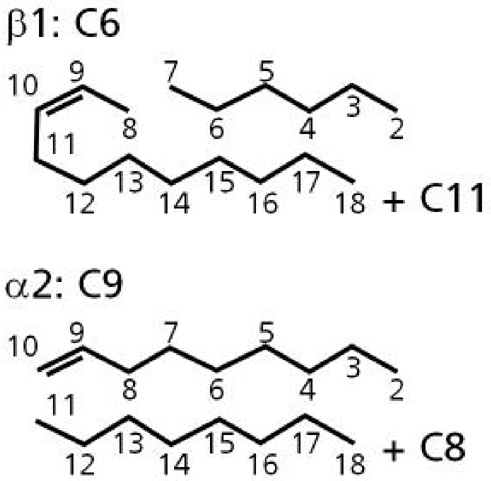

Fig. 3: Secondary cracking products of oleic acid molecule at predetermined breaking points (examples)

Moderate reaction conditions assumed, pure Cn saturated fatty acids (a saturated fatty acid with n C-atoms), would lead to the liquid alkane product components with yields monotonously decreasing from Cn-1 to C5 in the Organic Liquid Product (OLP). Like Fig. 4 shows, catalytic cracking of high oleic safflower oil at 450 °C over steam-activated carbon leads to a completely different pattern: there is a distinct peak at C8 to C11 in the alkane yield.

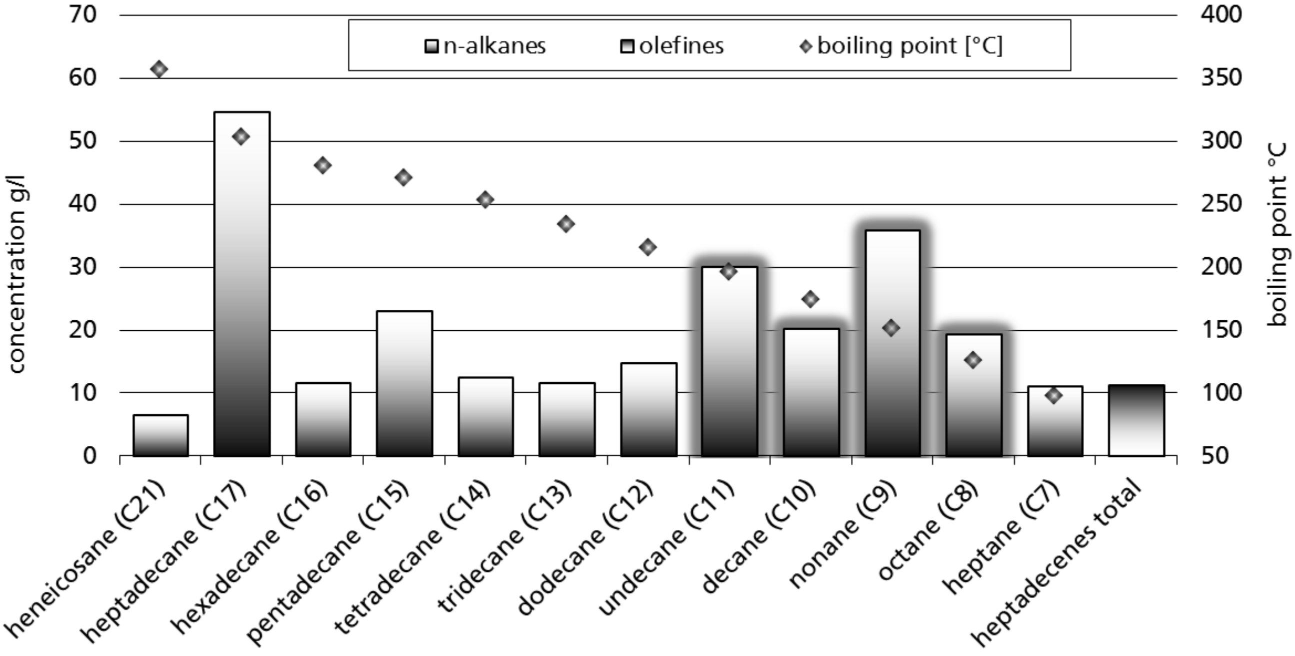

Fig. 4: Concentration of the main primary and secondary aliphatic catalytic cracking products in the organic liquid product of high-oleic safflower-oil (highlighted: main products of secondary cracking at predetermined breaking points)

Fig. 5 displays the overall yields and energetic yields of the experiment.

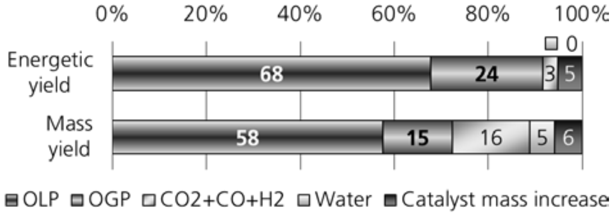

Fig. 5: Energetic yield and mass yield of the product sections of catalytic cracking of high-oleic safflower-oil

In a production scheme, the desired kerosene-distillation-range components would be seperated from the OLP's other components first. Then, the heavier components could be used for diesel fuel blending or – in case of the long-chain alkanes – be isomerized in order to fit into jet-fuel specifications.

3.2 Alkylated benzenes

With other plant oils like *Jatropha Curcas*-oil or plant oil wastes and especially with alternative, non-carbon-based microporous catalysts, remarkable amounts of alkylated benzenes can be produced [7,8]. Benzene and toluene were not detected; the typical chain-length of the branched alkyl is C4 to C11. They can be used for supplementing the aromatic content of bio-jet-fuel, which the products in most of the alternative process routes lack.

4. Conclusion

Catalytic cracking of plant oils over activated carbon and other microporous catalysts represents a novel route to produce blending components for bio-jet-fuel. Long-chain alkanes (esp. C15 and C17) for isomerization as well as shorter n-alkanes that fit the kerosene boiling range directly are produced. Alkylated benzenes are another product group that is required for jet fuel.

When algae oil, oils from arid land or waste oils and fats are processed, no issues with food production or rainforest consumption arise. Due to the robustness of the process (tolerant catalyst and feed evaporation), it is very well applicable for these low-quality feedstock varieties.

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