Upgrading Biodiesel into Oxygen-Free Gasoline: New Applications for the FCC-Process

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Abstract

Using vegetable oils as feedstock for fluid catalytic cracking is a promising and sustainable alternative to oils of fossil origin. Depending on the framework conditions, it may be more reasonable to use fatty acid methyl ester (FAME). For this work, different blends of FAME with vacuum gas oil (VGO) were mixed. At a mean riser temperature of 550°C, pure FAME yielded gasoline (45.7%), crack-gas (18.0%), light cycle oil (LCO) and residue (17.4%) and coke (4.6%). The oxygen contained in the biomass was converted to water (11.9%), CO (2.0%) and CO\textsubscript{2} (0.5%). This conversion is one of the key features when using the FCC technology with biomass. The obtained products are therefore free from oxygenates.

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1. Introduction

Carbon dioxide appears to be the most important anthropogenic greenhouse gas. Since the primary sources of CO\textsubscript{2} are the use of fossil fuels [1], one possible way to reduce emissions would be using fuels from renewable sources. Accordingly, the European Council passed a directive that endorses a mandatory target of a 20% share of energy from renewable sources overall and a mandatory 10% share of biofuels in transportation sector by 2020 [2].

Previous research has shown that vegetable oils are a promising feedstock for fluid catalytic cracking [3], [4], [5], [6]. One problem with raw vegetable oils is that they contain relatively high amounts of phospholipids (i.e. lecithin) and free fatty acids. Depending on the catalyst used and the operating
conditions, the phosphorus contained in the phospholipids may promote catalyst deactivation [7]. Free fatty acids, on the other hand, can cause corrosion inside the FCC plant or the related periphery [8].

Two feasible options to avoid problems are to maintain either a refinery for edible oils (at least capable of handling the steps of degumming and neutralizing), or a reactor for transesterification (to produce fatty acid methyl ester, FAME [9]). The process via FAME seems favorable, since the costs for the chemicals involved in both methods are comparable [10], whereas the glycerin that accrues during transesterification is a valuable by-product. Another advantage is the possibility of selling any excess FAME as biodiesel.

2. Experimental Setup

2.1. The Catalyst

For the cracking of the oil, a standard zeolite FCC catalyst was used. The catalyst was an equilibrium catalyst (e-cat) by Grace Davison (E-Space®). For more details, refer to Table 1 below.

Table 1. Specifications of the catalyst used

<table>
<thead>
<tr>
<th>Catalyst Manufacturer</th>
<th>Grace Davison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trade name</td>
<td>E-Space®</td>
</tr>
<tr>
<td>Type of catalyst</td>
<td>shape-selective zeolite</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>20 – 200 μm</td>
</tr>
<tr>
<td>Mean particle size</td>
<td>75 μm</td>
</tr>
</tbody>
</table>

2.2. The Feed

A commercially available FAME was used for the experiments. Fig. 1a shows the fatty acid composition. The pure FAME was blended with vacuum gas oil (VGO), the standard FCC feed, and mixtures of 0% (pure VGO), 20%, 50% and 100% (pure FAME) were prepared and processed.

2.3. The Pilot Plant

For the experiments, a continuously working FCC pilot plant (see Fig. 1b) was used. The different sections in the plant are the feed pre-heater, the riser (where the catalyst comes in contact with the feed and the cracking takes place), the regenerator (where the spent catalyst is regenerated) and the product gas condensation. All areas are kept under an inert gas atmosphere (nitrogen), except the regenerator (which needs oxygen to burn off the coke) [11].

The plant is constructed in an internal circulating design, thus the riser is inside the regenerator. This is a major difference to most other FCC plants, which have external circulation. The main advantages of internal vs. external circulation are:

- the compact design
- a simpler architecture (i.e. no slide valve for catalyst recirculation or cyclones are needed)
- desired heat coupling regenerator (exothermic combustion of coke) – riser (endothermic crack-reaction)
- the use of electric heating shells allows to set and control the cracking temperature precisely
The feed pre-heater is an electrically heated tubular oven. The feed is heated up to 300°C. The pressure drop caused by the length of the oven (9 m) helps to level any peaks in flow rate and thus assures a constant transport of the feed into the reactor.

Inside the reactor, the pre-heated oil comes in contact with the hot catalyst. This leads to vaporization of the oil. The gaseous feed molecules can then react with the catalyst particles. The cracking reactions produce many gaseous molecules, which in turn are responsible for the increase in volume. This effect causes an upward movement inside the riser. The thus created flow conveys the catalyst to the top. Here, the particle separator diverts the cat-flow to the regenerator. The product gas, on the other hand, leaves the reactor and is transported to the product gas condensation, where samples for analysis are taken.

The spent catalyst circulates internally to the regenerator. Since this area of the reactor is fluidized with air, a siphon (fluidized with nitrogen) is used to strip the catalyst on the one hand, and prevent the air from entering the product gas side on the other hand. The siphon also enables us to measure the catalyst circulation rate: when siphon fluidization is turned off, no further spent catalyst can enter the regenerator. Since there is still catalyst transported through the riser, the catalyst level in the regenerator drops. This is measured as a pressure drop, which in turn is converted into a circulation rate.

The regenerator is constructed as a stationary fluidized bed. Air is used as a fluidizing agent in order to burn off the coke which deposits on the catalyst during the cracking reaction. The average residence time in the regenerator is around 10 minutes.

The bottom section is built with a fluidization system as well. Like the siphon, this is used to strip the catalyst coming from the regenerator and to prevent the catalyst-flow from stopping.

3. Results

Each data point comprises of at least three single values which were averaged to improve statistical significance. Unless stated otherwise, all experiments were conducted at a mean riser temperature (average of $T_{\text{Riser,IN}}$ and $T_{\text{Riser,OUT}}$) of $T_{\text{Riser,avg}} = 550°C$. 
Fig. 2a shows an overview of the cracking results with FAME compared to VGO. The decrease in gasoline (-11%) and crack-gas (-5%) is mainly due to the formation of oxygen-compounds (+15%). All oxygen contained in the biomass is converted to either water (usually around 12%), which can easily separated, or CO and CO₂ (together around 3%). The data also shows an increase in heavier products (light cycle oil (LCO), residue and coke).

For a better comparison, Fig. 2b shows the above data corrected by the amount of oxygen compounds. The figure depicts a shift to heavier (higher boiling point) products (+4% in LCO & Residue, +1% in Coke). Since a VGO-optimized catalyst was used, this trend may change when adapted catalysts become available.

Fig. 2. (a) Comparison of 100% VGO to 100% FAME as an FCC feedstock, (b) data corrected by water, CO₂ and CO

Fig. 3a depicts in detail the change in lumps with variation to the feed composition. The total fuel yield (TFY) is the sum of all valuable products. As mentioned before, the decrease in total fuel yield is mainly due to the formation of water. Fig. 3b shows this rise as well as the increase in heavier products.

Fig. 3. Influence of FAME content of the feed on the (a) valuable products, (b) and on the side products

Fig. 4a shows the amount of olefins contained in the crack-gas. Interestingly, only propene is formed less (-2%). Regarding the other olefins, there is almost no change to observe. Considering the formation of water and other oxygen compounds (ca. 15% for pure FAME), these data actually correspond to an
increased formation of olefins. Fig. 4b shows the concentrations of the olefins in the crack-gas. The high concentration of olefins in the gas (68-76%) is a main advantage of the FCC technology.

Fig. 4. Olefins obtained with the Crack-Gas depending on FAME content of the feed, (a) feedbased and (b) gasbased

Fig. 5a shows the influence of a higher mean riser temperature on the product composition. As expected, there is an increase in gasoline (+2%) and crack-gas (+4%), and a decrease in heavier products (-4% for LCO & Residue, -2% for Coke). This shift towards lighter products is due to the kinetics of the cracking reaction. Fig. 5b shows that the olefins follow this general trend. The increased formation is seen best with propene (+1.9%) and 1-butene (+1.3%), less with 2-Butene (+0.7%) and ethane (+0.4%).

Fig. 5. Effect of an increased $T_{\text{Riser avg}}$ on (a) the product composition, (b) the olefins contained in the Crack-Gas

4. Conclusions

Cracking FAME is an interesting option to produce gasoline (and economically even more important olefins for the polymers-industry) in a sustainable way.

The main advantages when using the FCC technology are the high amounts of olefins in the crack-gas and the high octane number of the gasoline (in these FAME experiments, a RON of 100-105 was measured). But the main benefit of this catalytic conversion is the production of a fuel that is completely oxygen-free.
This means that the obtained bio-gasoline is neither hygroscopic (it thus can be stored in containers without a special seal) nor has solvent-like properties (which might damage gaskets or seals used especially in older cars).

Acknowledgements

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References


