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CATALYTIC CRACKING OF PURE FATTY ACIDS IN A CONTINUOUS SMALL SCALE PILOT PLANT

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ABSTRACT: Fluid catalytic cracking is one of the most important refinery processes for gasoline production. It could be shown in previous works that vegetable oils are a suitable feedstock for the FCC process. One of the most important criterions for biofuels is its profitability. Due to the high costs of virgin vegetable oils products from a "BIO-FCC" are expected to be considerably more expensive than petrol-derived products. Crude palm oil contains high amounts of free fatty acids which are removed during refining as so called palm fatty acid distillate (PFAD). The price of PFAD is approximately 50% of purified palm oil. All experiments were conducted in a fully continuous small scale pilot plant with internal CFB design.

Keywords: biofuel, catalytic conversion, circulating fluidized bed (CFB), palm oil, petrochemical substitute, renewable energies

1 INTRODUCTION

Crude oil is still the most important global energy carrier and a very important feedstock for chemical industries [1]. Nowadays it is mainly used for the production of heat, electricity, liquid and gaseous fuels as well as for the production of chemicals. Within the last decades an intense discussion about the risks of unrestricted use of crude oil and other fossil energy carriers has started: Many scientists see a connection between the rising atmospheric CO₂ concentration derived by the combustion from fossil energy carriers and the global warming [2].

As a possible solution technologies which substitute fossil energy carriers by renewable sources have gained importance within the last years. They implicate two major advantages over fossil fuels: They are CO₂-neutral and resources can be used sustainably. While the production of heat and electricity from renewable sources can already be considered as state-of-the-art, technologies for the production of liquid fuels and raw materials for the chemical industry are still under development. The use of biomass offers big potentials.

Fluid catalytic cracking (FCC) is one of the most important refinery processes for high octane gasoline production. Nearly every refinery worldwide operates an FCC-plant. It could be shown in previous works that vegetable oils are a suitable feedstock for the FCC process. Micro reactor tests were performed by Idem and Dupain. Canola and rapeseed oil were converted successfully to gasoline, a gaseous fraction, a higher boiling fraction, water and coke [3, 4].

At Vienna University of Technology Reichhold and Hofbauer designed and constructed a fully continuous small scale pilot plant with internal CFB design [5]. Preliminary tests with admixtures of vegetable oil to vacuum gasoil (VGO) were conducted by Reichhold [6, 7]. In further experiments pure vegetable oil was processed [8].

The objective of this paper was to test the suitability of pure fatty acids as feedstock for the FCC process. Dupain proposed that triglycerides are split in a first fast step in free fatty acids and glycerin with subsequent cracking [4]. Therefore no major difficulties were expected for the process. Experiments were performed

with palmitic acid C16:0, oleic acid C18:1 and a 50:50 mixture of these two fatty acids, following called POA.

One of the most important criterions for biofuels is its profitability. Due to the high costs of virgin vegetable oils products from a "BIO-FCC" are expected to be considerably more expensive than petrol-derived products. Crude palm oil contains high amounts of free fatty acids which are removed during refining as so called palm fatty acid distillate (PFAD). The price of PFAD is approximately 50% of purified palm oil (PPO).

Recently several studies of converting fatty acids and fatty acid rich vegetable oils to biodiesel via transesterification were conducted. In comparison with the standard transesterification process it is more sophisticated thus leading to higher costs [9]. On the contrary, for converting fatty acids by FCC no additional costs to vegetable oil feed are expected which gives this process an advantage.

2 EXPERIMENTAL

2.1 Small scale pilot plant

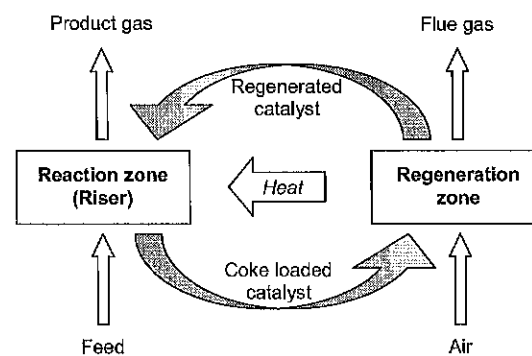


Figure 1: Principle of dual fluidized bed FCC

Fig. 1 depicts an overview of the process. A FCC plant consists of the two main parts: reactor (also called riser) and regenerator. Feed and regenerated catalyst enter the reaction zone where the cracking occurs and coke is deposited at the catalyst surface. Product gas

leaves the reactor while the coke loaded catalyst is transported to the regeneration zone. Here coke is burned with air. Regenerated hot catalyst flows to the reaction zone transporting heat.

All experiments were conducted in a fully continuous FCC pilot plant at Vienna University of Technology. In Fig. 2 a scheme of the used small scale pilot plant is shown. It is realized as an internal circulating fluidized bed which means that regenerator and reactor are arranged concentrically in one apparatus.

Feed is dosed by a gear pump and preheated in a tubular oven up to a temperature barely under boiling temperature (approximately 250 – 300°C) and enters the apparatus at the bottom of the riser. Here it comes in contact with the hot catalyst and evaporates instantaneously resulting in a strong upwards expansion. Due to this expansion catalyst is sucked into the riser and pneumatically transported to the top. All cracking reactions as well as coke formation and its depositing on the catalyst surface occur in the riser with a mean residence time of approximately 0.9 s. At the particle separator catalyst and gaseous product are separated. The product gas leaves the apparatus at the top. Due to the large increase in diameter from the riser to the upper part of the apparatus the fluidization velocity decreases under transportation velocity. Thus the catalyst goes down the return flow tube and enters the regenerator through a nitrogen fluidized siphon which acts as a gas barrier. In the regenerator coke is burned with air whereby the catalyst is regenerated. Emerging flue gas leaves the reactor laterally. The produced heat is required for the endothermic cracking reactions. It is transported via the hot bed material as well as direct heat transfer to the riser.

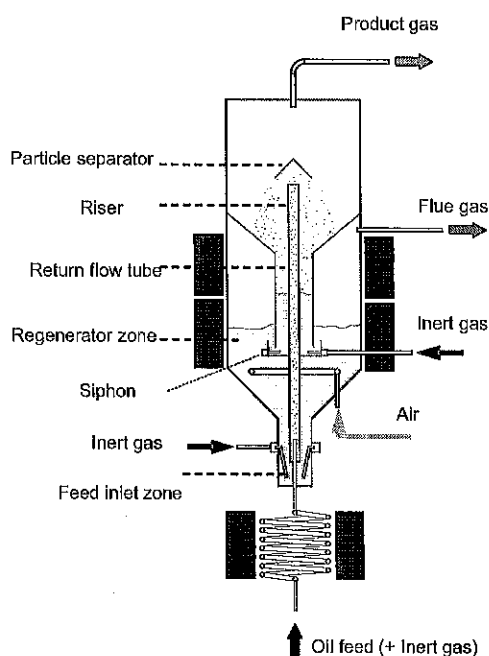


Figure 2: Scheme of the FCC pilot plant

Sufficient siphon fluidization is required in order to maintain circulation. Interrupting this fluidization results in a cut of transport of catalyst from the return flow tube to the regenerator. Thus the level in the return flow tube

increases while it decreases in the regenerator. Pressure measured at the bottom of the reactor decreases proportionately with the bed height allowing calculating the circulation rate during operation.

The product gas leaving the reactor is burned in a flare. For analyses purposes a branch current is extracted before the flare by a diaphragm pump and condensed in three intensive coolers. The incondensable crack gas flows through a gas sampling tube and a gas meter to the flare where it is combusted with the rest of the product.

A branch current of the flue gas is extracted and flows through a gas cooler to a gas analyzer.

In Table I some benchmark data from the FCC pilot plant is depicted.

Table I: Benchmark data of the FCC pilot plant

Height	2.5 m
Riser length	2.022 m
Riser diameter	0.0205 m
Regenerator diameter	0.18 m
Catalyst	Shape selective zeolite
Catalyst mass	9 - 11 kg
Catalyst spectrum	20 - 200 μm
Riser temperature	550 - 600°C
Regenerator temperature	590 - 650°C
Feed flow	1 - 3 l/h
Riser residence time	ca. 0.9 s
Pressure	Ambient
Fluidization bottom	1.5 Nl/min
Fluidization syphon	8 Nl/min
Fluidization regenerator	29 Nl/min
Fluidization velocity	16 vmf
Flue gas oxygen	1 - 2 vol%

2.2 Analysis

Gaseous and liquid products were analyzed separately with two gas chromatographs.

The gas chromatograph used for crack gas analysis consists of two capillary columns and two detectors. Hydrocarbons were detected by a flame ionization detector (FID), nitrogen and carbon dioxide were detected by a thermal conductivity detector (TCD). Some benchmark data can be found in table II.

Table II: Benchmark data of gas chromatograph

Gas-GC SHIMADZU GC-17A	
Carrier gas	Helium, 7 ml/min
Temperature program	15 min at 30°C ramp with 5°/min to 113°C dwell-time 50 min
Injector	200°C, splitless
Injection volume	100 μl
Column 1	Petrocol DH 150x0.25x1
Detector 1	FID, 200°C
Column 2	Carboplot P7 27.5x0.53x25
Detector 2	TCD, 80°C, 60 mA

Liquid products were analyzed conducting a simulated distillation (SimDist) using a gas chromatograph with a capillary column and a FID. Some benchmark data can be found in table III.

Table III: Benchmark data of SimDist

Gas-GC SHIMADZU GC-17A	
Carrier gas	Hydrogen, 2.3 ml/min
Temperature program	30°C ramp with 7°/min to 325°C dwell-time 20 min
Injector	325°C, split 1:20
Injection volume	1.6 µl
Column	Rxi-1ms 60x0.25x0.25
Detector	FID, 325°C

Additionally a PIONA analysis was conducted to obtain detailed information of the product composition and quality. ROZ and MOZ were determined by the FTIR fuel analyzer IROX 2000.

2.3 Feedstock and Catalyst

The experiments in the presented work were conducted with the two pure fatty acids palmitic acid C16:0 and oleic acid C18:1 and a 50:50 mixture of them.

Palmitic acid or hexadecanoic acid is the most widespread saturated fatty acid. At room temperature it consist of white wax like crystals with a melting point of 63°C. The boiling point lies between 351 and 352°C [inchem].

Oleic acid at room temperature is a colorless and odorless liquid that decomposes before reaching the boiling point [inchem].

The experiments were conducted with the commercial FCC equilibrium catalyst e-Ultima from the company Grace Davison. This is an acidic spray dried REUSY-catalyst which is partially coated with ZSM-5-zeolite crystals. It was already in use at the OMV refinery in Schwechat and extracted during the process from the FCC-plant. Thus there was no need to steam it to obtain a certain conversion level.

2.4. Definitions and calculations

For product characterization a lump model was used (Table IV). Gaseous and liquid fractions were separated by condensation. Oxygen contained in vegetable oils and fatty acids is mainly converted to water and small amounts of CO and CO₂. Water and liquid organic products can be easily separated by phase separation. The liquid organic phase is furthermore divided according to the boiling range in gasoline, light cycle oil (LCO) and Residue. In order to determine the coke lump the flue gas is analyzed by a gas analyzer for O₂ (paramagnetic

Table IV: Lump Model

Fraction	Lump	Composition, boiling range	Analysis method
Gas Fraction	Crack gas	C ₁ -C ₄	GC
Liquid fraction	Gasoline	<215°C	SimDist
	LCO	215 - 350°C	SimDist
	Residue	>350°C	SimDist
	Water		Gravimetric
Solid fraction	Coke		Flue gas composition

measurement method) as well as CO and CO₂ (infrared measurement method). The amount of coke is calculated

out of these values.

The lumps of the valuable products crack gas and gasoline based on feed are defined as total fuel yield X

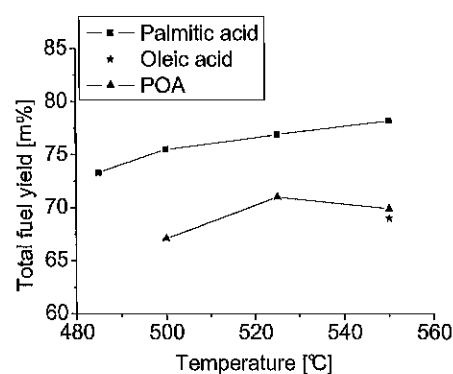
$$X = \frac{m_{Crackgas} + m_{Gasoline}}{m_{Feed}}$$

3 RESULTS

3.1 Fatty acids

The experiments lasted approximately six hours of steady state operation each. In this time three analysis suction of 15 minutes were done and averaged. Experiments with palmitic acid were conducted at four mean riser temperatures, 485, 500, 525 and 550°C, respectively. A steady state process could not be maintained with the 50:50 mixture of palmitic and oleic acid at 485°C probably due to the worse evaporation behavior of oleic acid. Three experiments were conducted at 500, 525 and 550°C, respectively. Pure oleic acid was processed at 550°C. The following figures depict the shift of the main product lumps and the composition as a function of the mean riser temperature. The regenerator temperature is dependent on the riser temperature and was between 500 and 610°C. Three liters feed per hour were processed.

The total fuel yield of palmitic acid increases with increasing temperature up to 78.2 m% (Fig. 3). Values for POA are generally lower with its maximum of 69.9 m% at 525°C. Oleic acid gives a total fuel yield slightly lower than POA.

**Figure 3:** Total fuel yield

The gasoline yield for palmitic acid decreases with increasing temperature (Fig. 4). Temperature shows only a slight influence on the gasoline trend of POA with a small maximum at 525°C. At 500°C the values for palmitic acid and POA are comparable. Oleic acid gives the highest gasoline yield at 550°C.

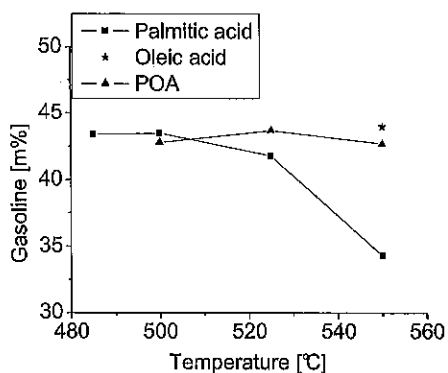


Figure 4: Gasoline yield

The yield of crack gas for palmitic acid rises approximately linearly between 485 and 525°C and increases stronger up to 550°C (Fig. 5). POA values are on a lower level and show an increase between 500 and 525°C, the value of 550°C is similar to the one at 525°C. The crack gas yield of oleic acid is slightly lower than the one for POA.

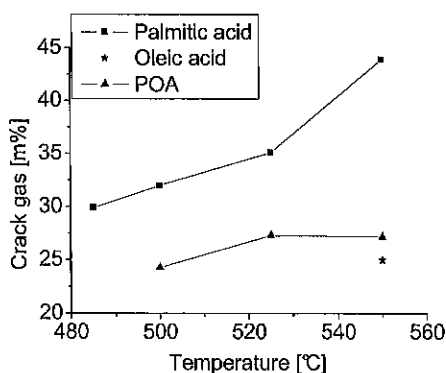


Figure 5: Crack gas yield

Light cycle oil and heavier components of palmitic acid show a decline with increasing temperature and the strongest decrease between 485 and 500°C (Fig. 6). The yield of POA lies generally on a higher level. It decreases from 500 to 525°C and increases slightly to 550°C. Oleic acid gives the highest value.

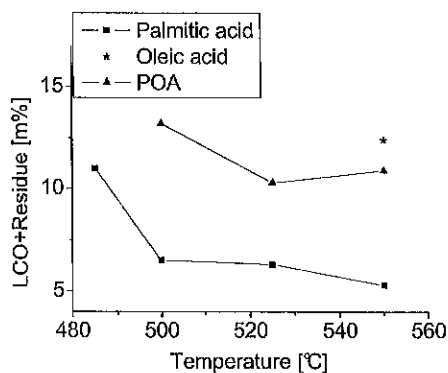


Figure 6: Light cycle oil and residue yield

The coke yield for both palmitic acid and POA shows a slight decrease with increasing temperature (Fig. 7). Oleic acid shows the highest coke amount.

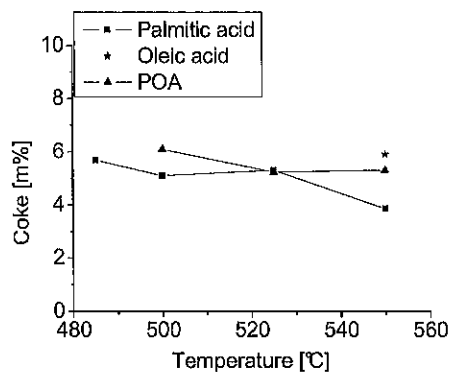


Figure 7: Coke yield

Water formation for palmitic acid is slightly less than for POA with no clear correlation to the temperature. Oleic acid at 550°C produces the same amount of water than palmitic acid.

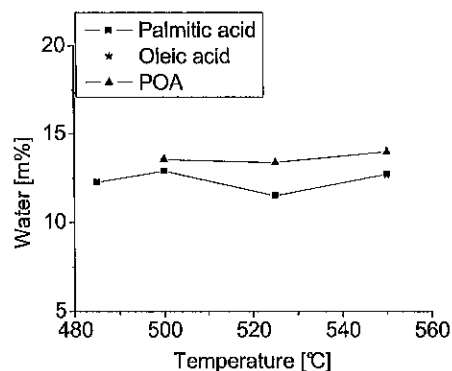


Figure 8: Water yield

Propene yields of palmitic acid and POA increase with increasing temperature (Fig 9.). The propene concentration in the crack gas stays approximately constant. As a consequence the increase is mainly caused due to the larger formation of crack gas. Oleic acid gives the lowest value; palmitic acid is on the highest level.

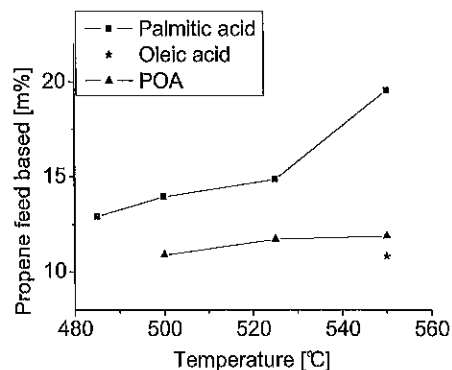


Figure 9: Propene yield feed based

The trend for ethene is similar to propene whereby the concentration in the crack gas is increasing also. The amount of ethene for oleic acid is slightly higher than for POA.

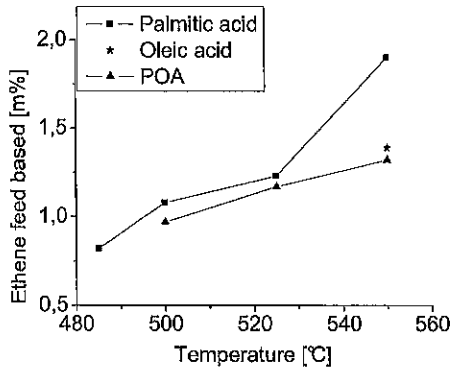


Figure 10: Ethene yield feed based

The trend for the main components of the gasoline fraction is depicted in the figures 11 and 12. For both palmitic acid and POA aromatics have the highest amount which is increasing distinctly with increasing temperature. Olefins, i-Paraffins and n-Paraffins decrease with higher temperatures. Naphthenes are vaguely constant for palmitic acid and decline for POA.

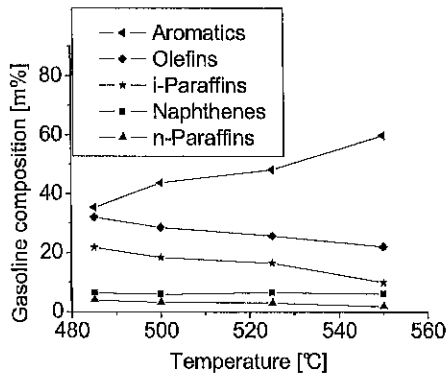


Figure 11: Composition of gasoline derived from palmitic acid

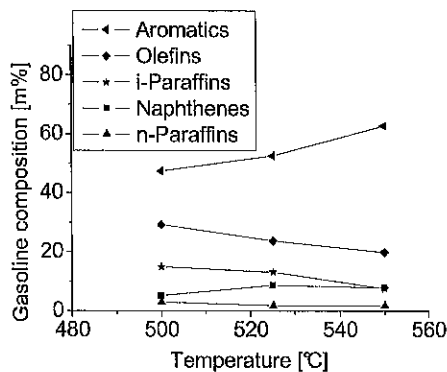


Figure 12: Composition of gasoline derived from POA

Both research and motor octane number increase with higher temperatures on high levels up to approximately 102 and 88, respectively (Fig. 13). The values from palmitic acid and POA are similar.

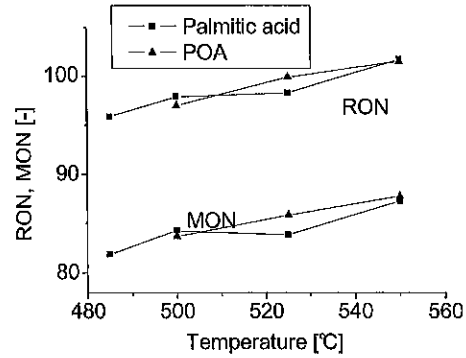


Figure 13: Research and motor octane numbers

3.2 Comparison with VGO and vegetable oils

In figure 14 a comparison of the main lumps between the fatty acids, vacuum gasoil and the three most common vegetable oils at 550°C is shown. Since VGO solely consists of hydro carbons it is oxygen free, neither water nor CO₂ and CO emerge. This fact has to be kept in mind when results between VGO and biogenous feeds are compared.

Gasoline formation for VGO and the vegetable oils is almost identical. Palmitic acid gives significantly less gasoline and oleic acid as well as POA slightly more. VGO and palmitic acid give the biggest crack gas lumps. Oleic acid and POA are approximately at the same level as the vegetable oils. VGO and palmitic acid give the highest total fuel yield followed by palm oil, oleic acid and POA. LCO and residue amounts vary clearly with the highest value for soybean oil and the lowest for palmitic acid. Coke formation for all feeds and water formation for the biogenous feeds is comparable.

The product spectrum of Palmitic acid stands out with lower gasoline, LCO plus residue and coke amounts and significantly more crack gas. This may be due to the saturation of the fatty acid. POA and palm oil give comparable results. This was expected since palmitic and oleic acid are the main fatty acids of palm oil.

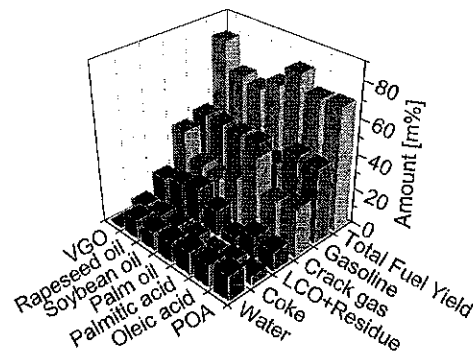


Figure 14: Comparison with VGO and vegetable oils at 550°C

4 CONCLUSIONS

Fatty acids are a very promising feedstock for the FCC process. They could be converted to high octane and oxygen free gasoline as well as to crack gas with high olefin content. The experiments could be conducted between 485 and 550°C without major problems. Due to the low price PFAD is a very interesting alternative to virgin vegetable oils. An interesting application would be co-processing in existing FCC plants.

POA (50 m% palmitic acid, 50 m% oleic acid) gives very similar results to comparable experiments with palm oil. It is suggested that the breakdown of triglycerides as a first step of vegetable oil conversion has no major influence on the overall process.

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