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PROCESSING OF PURE VEGETABLE OILS IN A CONTINUOUS FCC PILOT PLANT

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Abstract

The basic objective of the presented work is the application of vegetable oils as an alternative CO₂-neutral feedstock for fluid catalytic cracking (FCC). The experimental test program was conducted in a fully continuously operated FCC pilot plant with intern CFB-design at Vienna University of Technology. Vegetable oils with the highest global production (soy bean oil, palm oil and rapeseed oil) were used. The addition of vegetable oil had hardly any influence on the cracking process. The gasoline achieved is oxygen free at high octane numbers.

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 and liquid and gaseous fuels as well as for the production of chemicals. Within the last decades an extensive 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 sustainable. 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 are still in a stage of development. Especially the use of biomass offers big potentials.

Currently fermentation of glucose or starch to bioethanol and transesterification of vegetable oils to biodiesel are the most widespread technologies for the production of biofuels from renewable sources (3, 4, 5, 6). In recent studies alternative processes for biofuel production were investigated. Developments have been gained in the field of Biomass gasification with downstream Fischer-Tropsch synthesis for the production of a high paraffinic diesel (7).

Fluid catalytic cracking (FCC) of vegetable oils is a hardly known technology to produce biogasoline, gaseous olefins and light cycle oil (LCO), a blending

component for Diesel. The products are practically oxygen free. The gasoline fraction has a high octane number, thus it can be used in conventional engines without adaption. In refinery technology the FCC-process is the most important process for the production of high octane gasoline. A plant can be found almost in every refinery. Co-feeding of vegetable oils with common feedstock like vacuum gasoil (VGO) in existing units offers high potentials (8).

Basic studies of catalytic cracking of vegetable oils in micro reactor scale were conducted by various researchers with promising results (9,10).

At Vienna University of Technology a fully continuous FCC pilot-plant with internal CFB design was designed and constructed by Reichhold and Hofbauer (11). Preliminary tests with admixtures of rapeseed oil and used frying oils to Vacuum gasoil (VGO) were conducted by Reichhold (12, 13). In further experiments the vegetable oil content was enhanced (14). The objective of this paper was to test the suitability of three vegetable oils (soy bean oil, palm oil and rapeseed oil) as feedstock for the FCC-process. Therefore the vegetable oils were added in steps of 20 % to the conventional feedstock, up to 100 % addition. During the test runs the influence of the vegetable oil on the cracking process as well as the shift of the product spectrum were investigated. Finally the quality of the gained gasoline was evaluated through measuring octane numbers (RON, MON) and the composition via PIONA as well as oxidation stability.

Experimental Setup

Figure 1 gives a schematic overview of the fully continuous FCC pilot plant used for the experiments. Some benchmark data can be found in Table 1.

An FCC-unit consists of two main parts: the reactor (also called riser) and the regenerator. In the internal CFB system that was used for the experiments both parts are integrated into one apparatus with the riser concentrically arranged in the regenerator. The major advantages are the compact dimensions and the improved heat-coupling between regenerator and riser.

The feed is dosed by a gear pump and preheated in a tubular oven up to approximately 250°C and enters the riser through the feed pipe. Through contact with the hot catalyst it evaporates instantaneously. Due to the large upwards expansion the catalyst is sucked into the inlet of the riser. At the outlet the catalyst is separated from the product gas by a particle separator. The catalyst slips through a return flow tube and a nitrogen fluidized siphon into the regenerator, where the produced coke is burned with air. Through the combustion the reaction heat is provided for the endothermic cracking. The product gas leaves the reactor at the top through the product gas pipe and is then burned in a flare. For analysis purposes a branch current is sucked off the product gas pipe and condensed. Samples of the remaining gas are collected in a gas-sampling tube. Both liquid and gaseous samples are analyzed by means of gas chromatographs. The flue gas from the regenerator is analyzed for the CO₂, CO and O₂ content by a gas analyzer.

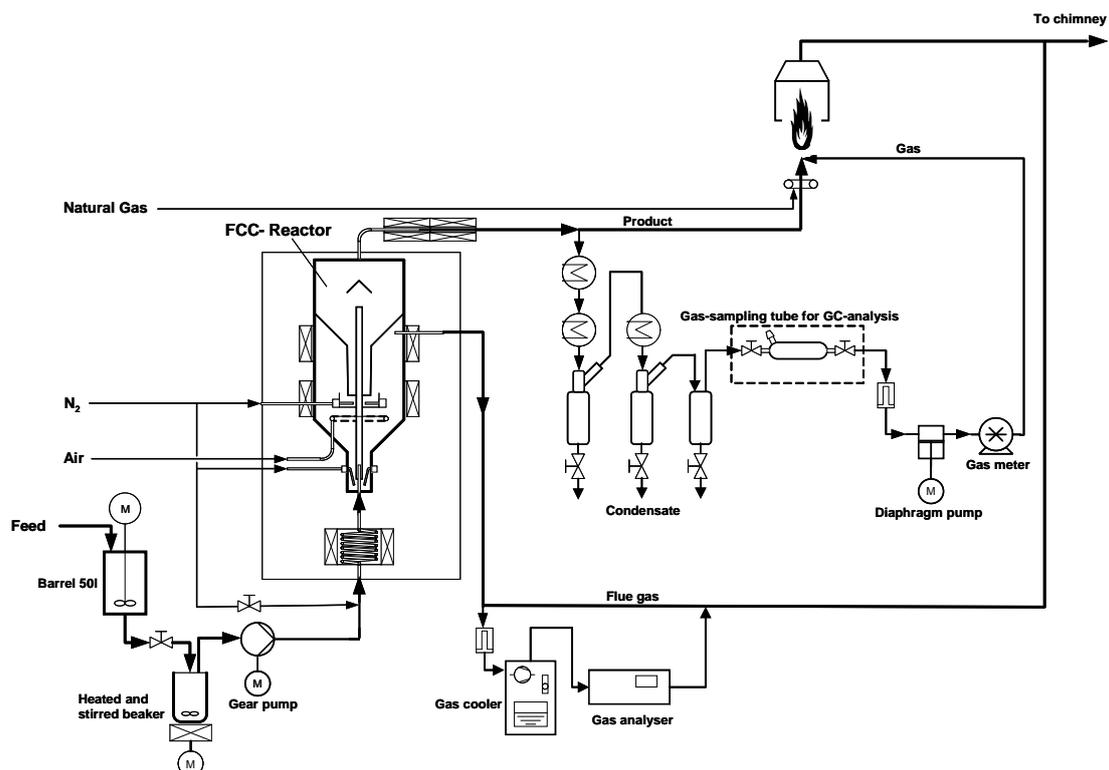


Figure 1: Scheme of the FCC pilot plant with periphery

Table 1: Basic 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 NI/min
Fluidization syphon	8 NI/min
Fluidization regenerator	29 NI/min
Fluidization velocity	16 v_{mf}
Flue gas oxygen	1 - 2 vol%

To enable continuous circulation a siphon and a fluidized feed inlet zone – both fluidized by nitrogen – are required. A further important role of these devices is their function as gas barrier between riser and regenerator.

To determine the gas leakages between reaction and regeneration zone tracer gas tests were performed at operation temperature. In each case three out of the four fluidizations of the plant – riser, regenerator, siphon

and feed inlet zone – were fluidized with nitrogen and the fourth was fluidized with CO₂. This was performed for each fluidization. The CO₂ content was determined with a gas analyser in the product and flue gas, i. e. in the reactor and regenerator.

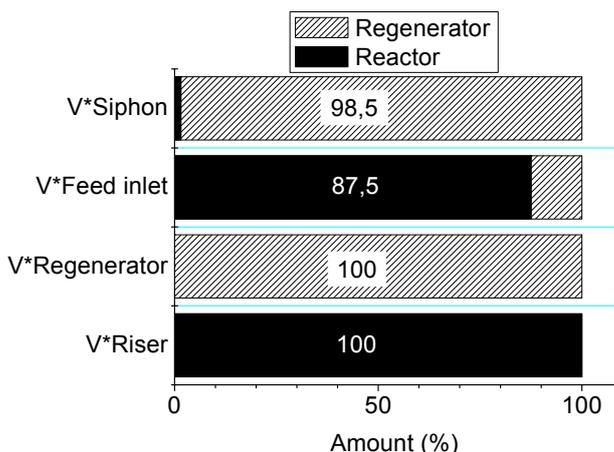


Figure 2: Distribution of fluidization gases between reactor and regenerator

Figure 2 shows that the fluidization air in the regenerator does not attain into the reactor where it would combust the products. On the other hand the riser fluids do not get into the regenerator which means that no vaporized feed or products reach the regenerator where they would be combusted. The main part of the siphon fluidization gets into the regenerator while most of the feed inlet zone fluidization attains into the riser.

Feedstock and catalyst

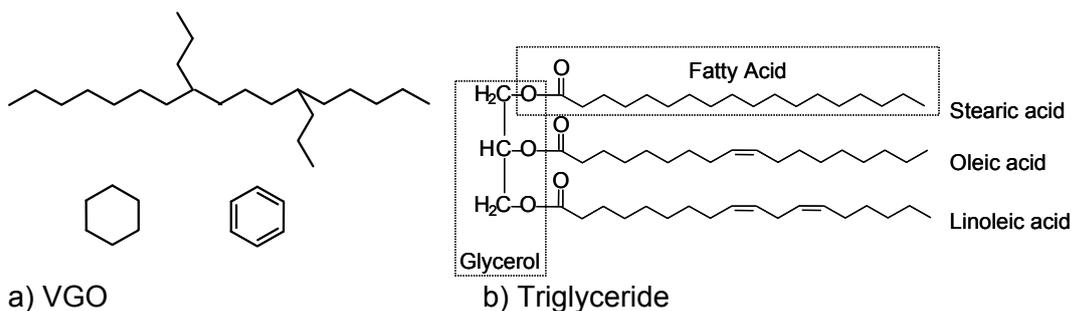


Figure 3: Structure of VGO and triglycerides

VGO – the top product from vacuum distillation with a boiling range between 350 and 650°C – is the standard feed for FCC plants. It consists mainly of paraffins, naphthenes and aromatics. A low sulfur content to obtain long catalyst lifetime is achieved by hydro treating (Figure 3a).

Vegetable oils mainly consist of triglycerides which are glycerin bodies with three fatty acid chains of different chain length and degree of saturation (Figure 3b).

The experiments were conducted with the commercial FCC catalyst equilibrium catalyst 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-cracker. Thus there was no need to steam it.

Definition and calculations

To characterize the product a 5-Lump model (Table 2) is used. The liquid phase is separated from the gaseous phase by condensation. When processing vegetable oils, water emerges from the oxygen in the triglycerides. It can be separated easily

from the liquid organic phase by phase separation. The organic phase is further analyzed by means of a simulated distillation in a gas chromatograph and divided into gasoline (boiling range <215°C), Light cycle oil (LCO, boiling range 215-350°C) and residue (boiling range > 350°C). The coke yield is calculated from the regenerator flue gas composition.

Table 2: 5-Lump model

Fraction	Lump	Composition/ Boiling	Analysis method
Gas fraction	CO ₂		Gas chromatography
	Crack gas	C1- C4	Gas chromatography
Liquid fraction	Gasoline	< 215°C	SimDist
	Light cycle oil (LCO)	215 – 350°C	SimDist
	Residue	> 350°C	SimDist
	Water	100 °C	Gravimetric
Solid fraction	Coke		Regenerator emissions (paramagnetic, infrared)

The conversion X is defined as the sum of gasoline and crack gas, the most valuable products.

$$X = \frac{m_{Crackgas} + m_{Gasoline}}{m_{Feed}} \quad (1)$$

Results

The experiments lasted approximately six hours each. During this time three analyses over a time range of 15 minutes were done and averaged. The mean riser temperature was set to 550°C which leads to a mean regenerator temperature of 590 to 600°C. The following figures depict the shift of the main product lumps as a function of the vegetable oil admixtures to VGO. The conversion decreases at higher ratios of vegetable oils (Figure 4). The best results could be achieved with palm oil followed by rapeseed oil. The gasoline yield stays roughly constant while the crack gas yield decreases. Soy bean oil shows the highest decline, palm oil the lowest.

The amount of LCO+Residue increases for soybean oil and rapeseed oil while for palm oil no essential alteration can be observed (Figure 5). The coke yield stays roughly constant for all three tested vegetable oils. Water and CO₂ are formed by the oxygen in the triglycerides of the vegetable oils. Thus their content is zero when processing VGO. Both substances show a linear increase. The formation of water is favored by catalytic cracking.

In Figure 6 the trends from the valuable gas components propene and ethene are depicted. The concentration in the gaseous phase is increasing while the absolute amount is decreasing due to the decline of the gas lump. For propene palm oil followed by rapeseed oil show the best results.

The research octane number depicted in Figure 7 shows a slightly increasing trend for all three oil up to values of approximately 100. The motor octane number decreases marginally. For all three oils the oxidation stability of the gasoline

increases. According to DIN EN228 a value of 360 is required which can be reached without any further refinement steps with higher vegetable oil admixtures.

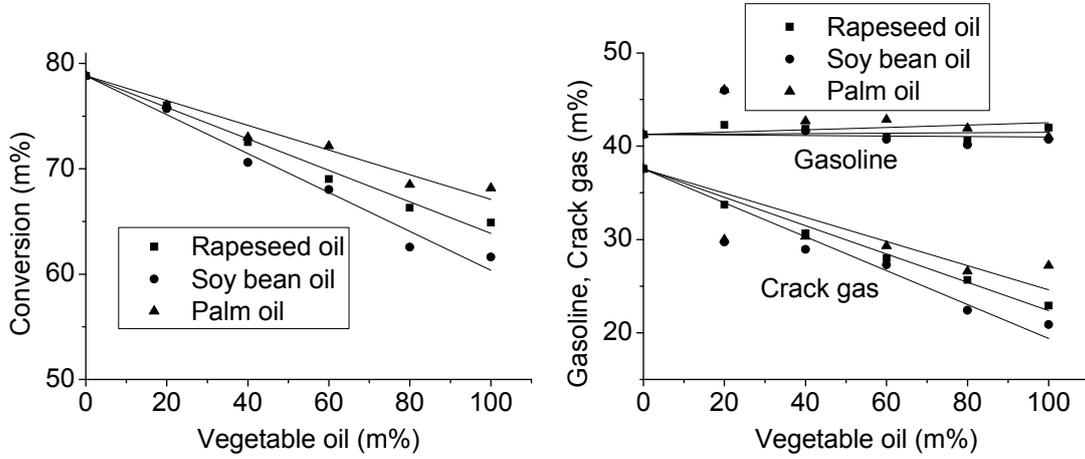


Figure 4: Conversion; Gasoline and Crack gas yields

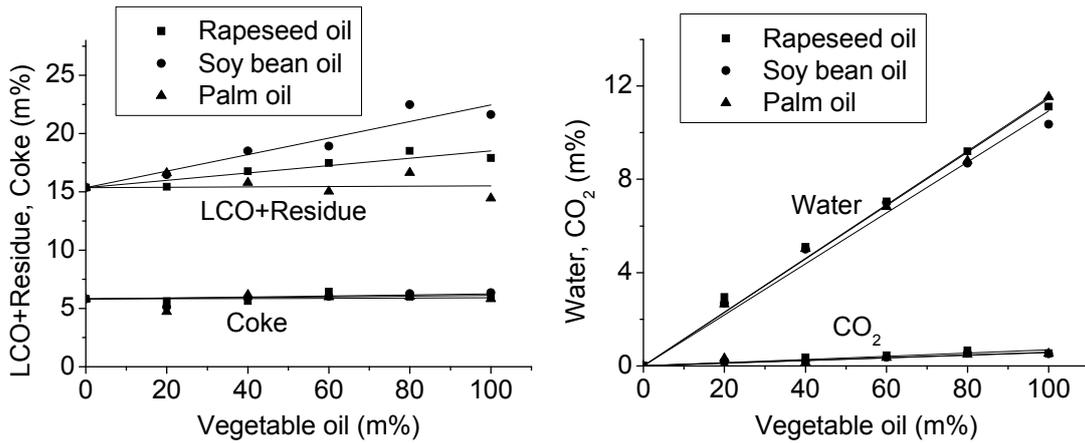


Figure 5: LCO+Residue and Coke; Water and CO₂ yields

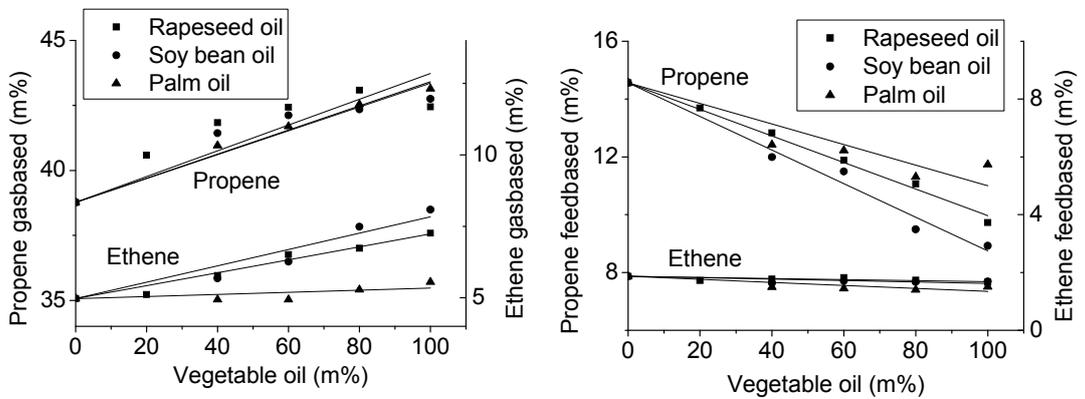


Figure 6: Propene and Ethene yields, gas based and feed based

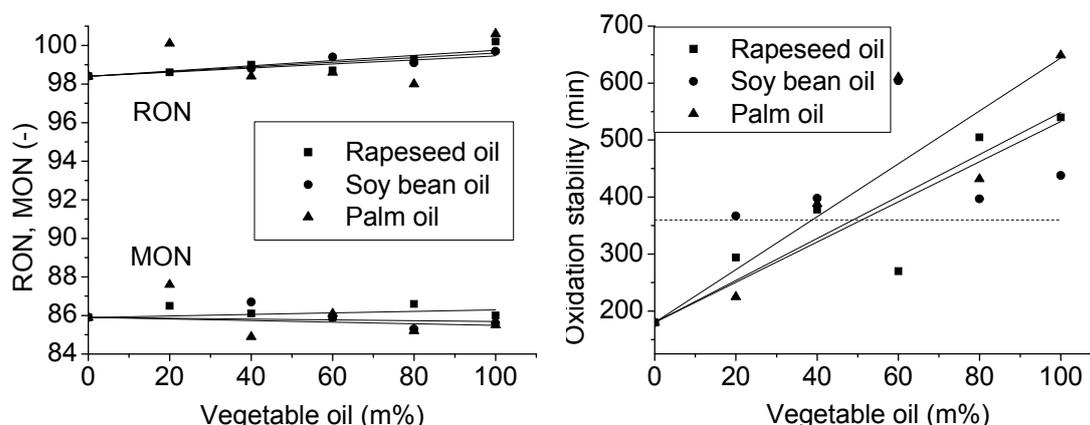


Figure 7: Research and Motor octane number; Oxidation stability

Table 3: Gasoline composition

Gasoline composition (m%)	VGO	Rapeseed oil	Soy bean oil	Palm oil
highboiling components	0,6	0,7	1,0	0,7
aromatics	54,0	63,7	60,5	53,3
polynaphthenes	0,2	0,3	0,4	0,1
olefinic naphthenes	4,5	8,7	9,1	5,9
naphthenes	6,4	3,5	4,3	5,0
iso-olefins	12,7	12,4	7,9	8,2
n-olefins	7,0	4,6	3,1	3,2
i-paraffines	12,4	3,8	9,3	17,4
n-paraffines	2,2	2,4	4,4	6,1

Table 3 gives an overview of the gasoline composition with different feeds via PIONA analysis. All samples show a high amount of aromatics which ensures high octane numbers. Gasoline achieved from palm oil shows the lowest alteration in comparison to VGO gasoline.

Conclusions

Mixtures of VGO and vegetable oils as well as pure vegetable oils could be processed successfully in a continuously working FCC pilot plant without difficulties. No major adaption was necessary. The obtained gasoline was characterized by high research octane numbers between 98 and 101 with a slight increase for higher vegetable oil amounts. The oxidation stability showed a considerable increase with higher vegetable oil admixtures. In contrast to biodiesel or bioethanol the liquid product is practically oxygen free.

The decrease in conversion can be mainly explained by the oxygen content of the vegetable oils. Oxygen was mainly converted to water. Only small amounts of CO₂ and CO emerged. In general palm oil showed the best results which may be due to the higher saturation of the fatty acid chains.

One of the most important advantages of the presented technology is the existence of large scaled plants in almost every refinery. With relatively small changes these devices could be used for so called co-processing (processing mixtures of standard crude oil derived feed and vegetable oils). Due to the chemical resemblance of bio

gasoline to conventional fuel gained via FCC it can be used without any modifications in standard automotive engines. Furthermore the high amounts of propene and ethene can be used to produce polymers out of renewable resources.

Acknowledgement

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