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PRODUCTION OF GASOLINE AND GASEOUS OLEFINS: CATALYTIC CO-CRACKING OF PYROLYSIS OIL RESIDUE

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ABSTRACT

Co-processing of biomass in petroleum refineries is a promising approach for biofuel production. In this work fluid catalytic cracking of residue from a co-pyrolysis with sawdust and VGO (1:2) was investigated. The pyrolysis oil residue with a boiling range bigger than 350 °C was mixed in different ratios with VGO and could be processed successfully up to 20 m%. Crack gas amounts increased while gasoline and total fuel yields decreased compared to VGO cracking. The gasoline obtained has a high octane number and is oxygen free.

INTRODUCTION

For the last decades crude oil was the most important raw material for the production of transport fuels. This leads to several problems like the dependence on politically unstable countries and the emission of huge amounts of fossil CO₂. Many scientists see a correlation between global warming and the increase in CO₂ concentration in the atmosphere (1). As a consequence new ways to substitute fossil fuels by renewable fuels have been investigated in the last years. Currently the production of so called first generation biofuels like bio ethanol and biodiesel can be considered as state-of-the-art technologies with considerable production capacities worldwide (2, 3). A disadvantage is that these fuels are derived from agricultural products which lead to a food vs. fuel dilemma (4).

Second generation biofuels made of lignocellulosic biomass from forestry as well as agricultural and industrial waste are not in competition with food. Gasification with downstream Fischer Tropsch synthesis has been investigated extensively (5-7). However, high investment costs lead to high fuel prices. In contrast, co-processing biomass with FCC-plants in existing crude oil refineries requires only little additional investments. Due to the very large scale the conversion process is highly efficient and existing downstream facilities for product upgrading can be used (8).

The suitability of the FCC-process for vegetable oils and used cooking oils has been shown by several researchers with promising results (9-11). The use of

lignocellulosic feed requires prior liquefaction. Bio oil obtained from flash pyrolysis is an interesting possibility for co-processing. Due to high oxygen and water content it is not miscible with VGO and needs upgrading associated with additional costs (12). Alternatively, bio oil can be in situ upgraded by introducing catalysts during pyrolysis (8).

In literature some experimental results with different pyrolysis oils as FCC feedstock can be found. All show the tendency to high coke formation and reactor plugging if they are processed in high concentrations (8, 12).

A new approach is co-pyrolysis. VGO is heated up in a stirred tank reactor and biomass is added. Released inorganic substances from biomass decomposition act catalytically. Thereby a part of the VGO is cracked mainly to diesel as well as gasoline and gases. These products leave the reactor. In this paper the suitability of a co-pyrolysis residue (boiling range 350°C plus) in admixtures with VGO in an FCC-plant is investigated.

EXPERIMENTAL

Small scale pilot plant

An FCC plant consists of the two main parts: reactor (usually constructed as riser), and regenerator. All experiments were conducted in a fully continuous FCC pilot plant at Vienna University of Technology. An internal circulating fluidized bed was used which means that regenerator and reactor are arranged concentrically in one apparatus. In Figure 1 a scheme of the apparatus and the periphery is shown, Table 1 comprises some benchmark data.

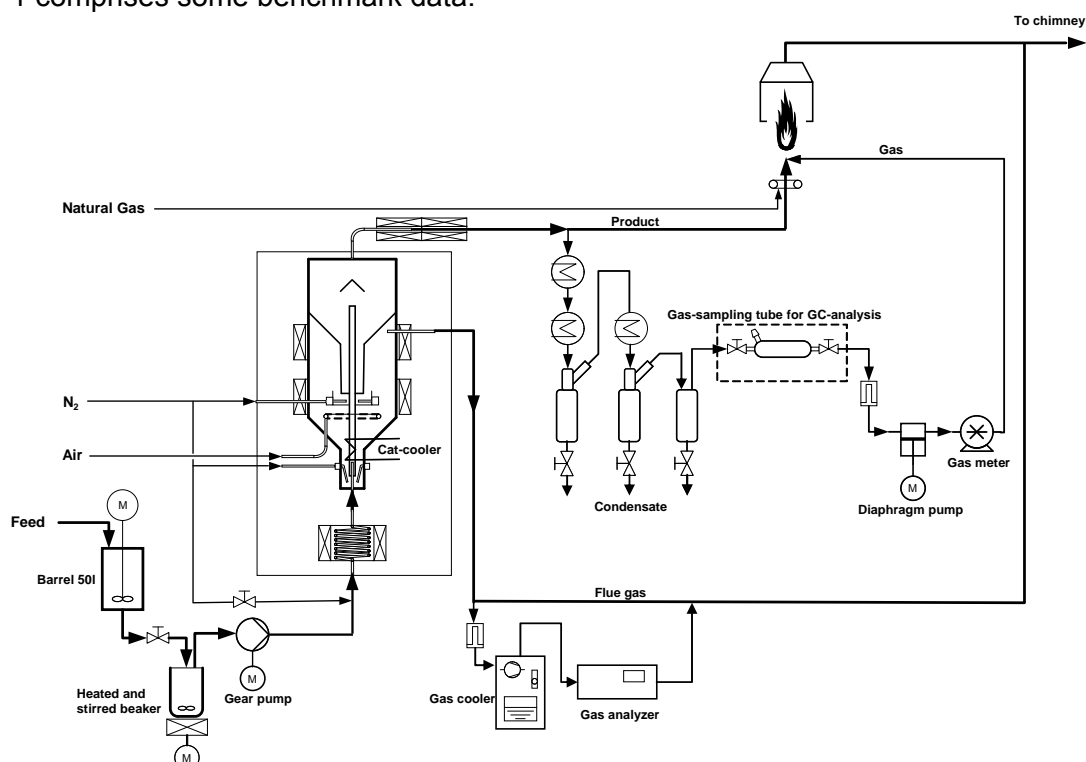


Figure 1: Scheme of the FCC pilot plant and periphery

Feed is dosed by a gear- or a peristaltic pump and preheated in a tubular oven to a temperature barely under boiling temperature (approximately 280–320 °C) and enters the apparatus at the bottom of the riser. Due to the contact with the hot catalyst it evaporates instantaneously resulting in a strong upwards expansion. Thereby catalyst is sucked into the riser and pneumatically transported to the top. All cracking reactions as well as coke formation and deposition on the catalyst surface occur in the riser within a mean residence time of approximately 0.9 s. At the particle separator catalyst and products are separated. The product gas leaves the apparatus at the top. Due to the large difference in diameter from the riser to the upper part of the apparatus the fluidization velocity decreases under transportation velocity. Thus, the catalyst flows 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 heat generated is required for the endothermic cracking reactions. It is transported via the hot bed material as well as direct heat transfer to the riser. Feedstocks which yield more coke, and thus to a high catalyst temperature in the regenerator, require a cooler in the bottom part to adjust the riser temperature.

Table 1: Benchmark data of the FCC pilot plant

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

Sufficient siphon fluidization is required in order to maintain circulation. Interrupting this fluidization results in a breakdown of the circulation. As a result 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 whereby the circulation rate can be calculated during operation.

The product gas is burned in a flare. For analyses purposes a branch current is sucked off 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 and is then combusted with the rest of the product. The regenerator flue gas is determined by a gas analyzer.

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 are detected by a flame ionization detector (FID), nitrogen and carbon dioxide are detected by a thermal conductivity

detector (TCD). Liquid products were analyzed conducting a simulated distillation (SimDist) using a gas chromatograph with a capillary column and an FID.

Additionally a PIONA analysis was conducted to obtain detailed information of the product composition and quality. RON and MON were calculated out of these results.

Feedstock and Catalyst

The experiments were conducted with different mixtures of VGO and residue from a co-pyrolysis from VGO and lignocellulosic biomass. Both feeds were provided by the OMV AG. VGO is the top product of the vacuum distillation with a boiling range between 350 and 650°C. It consists mainly of paraffins, naphtenes und aromatics. A low sulfur content to obtain long catalyst lifetime is achieved by hydro treating (Figure 2). The co-pyrolysis was conducted in a batch stirred tank reactor under atmospheric pressure. VGO was heated to approximately 350 °C and 33 m% biomass (sawdust) was added. The lignocelluloses started to decompose immediately to gaseous and liquid products, coke, and inorganic compounds. These inorganic substances (mainly salts) act catalytically and enable cracking of a part of the VGO. All substances with a boiling range below reactor temperature (mainly diesel with a cetane number of approximately 40 as well as gasoline, gases, and water) leave the reactor. The remaining residue and coke are separated by a centrifuge. According to C14 analysis the residue contains a certain amount of biomass derived substances. Only small amounts of the oxygen from the biomass remain in the residue. Table 2 shows the elementary analysis. Detailed analyses of the co-pyrolysis residue are confidential and cannot be published. In this paper the suitability of this residue (boiling range 350°C plus) in admixtures with VGO in an FCC-plant is investigated.

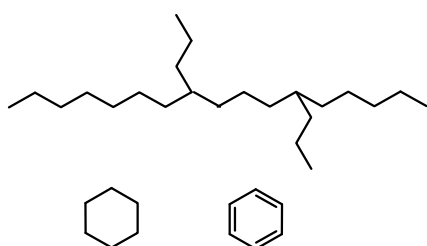


Figure 2: The main components of VGO

Table 2: Composition of the co-pyrolysis residue

Nitrogen	0.3	[m%]
Carbon	84.7	[m%]
Hydrogen	11.1	[m%]
Sulfur	<0.1	[m%]
Oxygen	1.8	[m%]
Ash	1.576	[m%]
Water	<0.1	[m%]

The commercial FCC equilibrium catalyst E-Space from the company Grace Davison was used. It 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.

Definitions and calculations

For product characterization a lump model was used (Table 3). Gaseous and liquid fractions were separated by condensation. Water and liquid organic products can be easily separated by phase separation. The liquid organic phase was divided furthermore according to the boiling range in gasoline, light cycle oil (LCO) and residue. In order to determine the coke lump the flue gas was analyzed by a gas analyzer for O₂ (paramagnetic measurement method) as well as CO and CO₂ (infrared measurement method). The amount of coke is calculated out of these values.

Table 3: The six Lump Model

Fraction	Lump	Composition, Boiling range	Analysis method
Gas Fraction	Crack gas	C1-C4	GC
Liquid fraction	Gasoline	<215°C	SimDist
	LCO	215 - 320°C	SimDist
	Residue	>320°C	SimDist
	Water		Gravimetric
Solid fraction	Coke		Flue gas composition

The total fuel yield X is defined as:

$$TFY = \frac{m_{Crack\ gas} + m_{Gasoline}}{m_{Feed}}$$

RESULTS

Experiments lasted about six hours each in steady state operation. Three sample periods of 15 minutes were made per run and analyses values were averaged. The riser temperature was set to 550 °C.

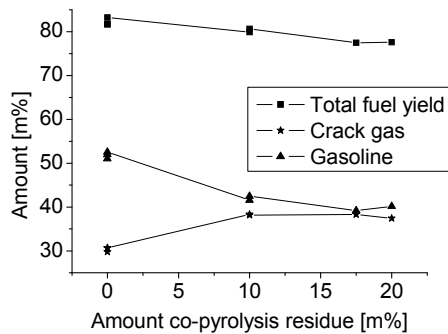


Figure 3: Influence of co-pyrolysis amount on total fuel yield, crack gas, and gasoline

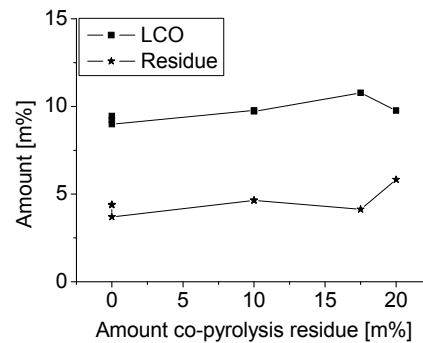


Figure 4: Influence of co-pyrolysis amount on light cycle oil and residue

Figure 3 depicts the total fuel yield. It decreases from approximately 82.5 m% for VGO to 77.5 m% with 20 m% admixture of pyrolysis residue. The gasoline yield decreases significantly from approximately 52 m% to 39 m% with a pyrolysis residue content of 17.5 m% and increases to 40 m% with 20 m% pyrolysis residue. Crack

gas rises clearly from 31 m% to a maximum of 38 m% between 10 and 17.5 m% pyrolysis residue addition and decreases slightly to 37.5 m% at a 20 m% admixture. LCO increases slightly with a maximum at 17.5 m% pyrolysis residue addition. Approximately 4 m% residue is formed with a clearly higher value at 20 m% pyrolysis residue admixture (Figure 4).

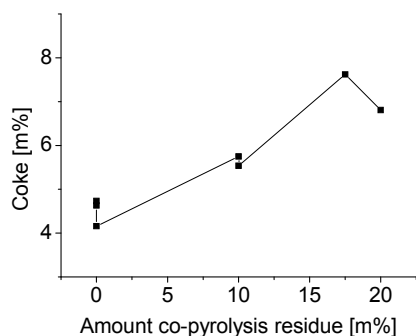


Figure 5: Influence of co-pyrolysis amount on coke

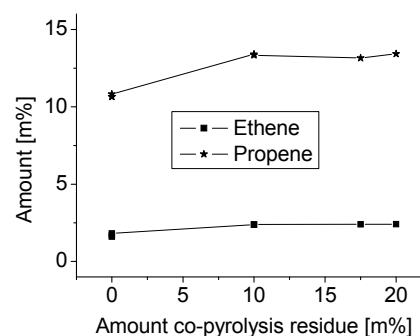


Figure 6: Influence of co-pyrolysis amount on ethene and propene

Coke amounts increase strongly with higher pyrolysis residue ratios with a maximum at 17.5 m% addition (Figure 5). Ethene and propene increase with increasing pyrolysis residue admixture. This is mainly caused by higher crack gas yield, concentration of gas components stays roughly constant (Figure 6).

The C/O ratio for experiments with pyrolysis residue addition was higher than for VGO experiments (Figure 7). Figure 8 shows the gasoline composition for three samples with different pyrolysis residue amounts in the feedstock. Naphtenes and iso-paraffins concentrations are less with admixtures, more aromatics are formed. N-paraffins and olefins stay roughly constant.

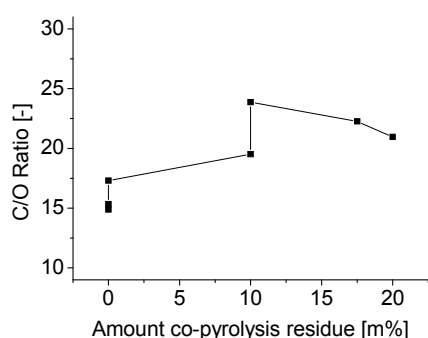


Figure 7: Influence of co-pyrolysis amount on the catalyst/oil ratio

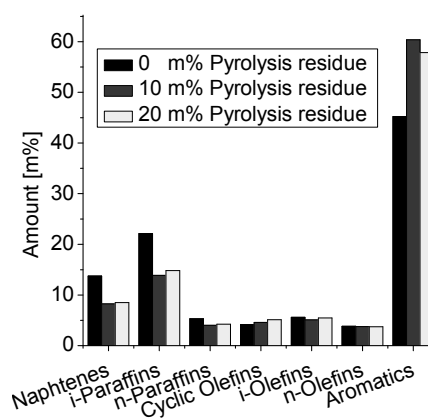


Figure 8: Gasoline composition with different amounts of co-pyrolysis residue

Table 4 depicts some gasoline characteristics. Research octane numbers (RON) are generally at a high level with bigger values for experiments with pyrolysis residue

addition. Motor octane numbers (MON) show an opposite trend. Benzene (like aromatics in general) increases at higher pyrolysis residue ratios. The caloric value for all samples is at a similar level. Gasoline from feedstock with addition contains less hydrogen. Further on, density and thus average molecular weight are slightly higher.

Table 4: Gasoline characteristics

Amount pyrolysis oil	0	10	20	[m%]
RON	101.8	104.4	103.2	[-]
MON	90.5	89.5	88.2	[-]
Benzene	0.99	1.64	1.56	[m%]
Caloric value	42.85	42.19	42.28	[MJ/kg]
C:H Ratio	0.57:1	0.62:1	0.61:1	[-]
Density	763.5	791.2	788.0	[kg/m ³]
Average molecular weight	104.2	106.3	106.4	[g/mol]

CONCLUSIONS

Admixtures of VGO and co-pyrolysis residue up to 20 m% could be converted successfully in a fully continuous FCC pilot plant for several hours in steady state operation. No major adaption was necessary. Higher pyrolysis residue contents led to more crack gas and less gasoline, resulting in a decrease in total fuel yield. The product quality was very high with RON clearly over 100 and MON around 90. Due to the chemical similarity (the product is oxygen free) it can substitute regular gasoline in any percentage without limitation.

VGO experiments could be conducted without catalyst cooling in the regenerator bottom. Due to the bigger coke yield with pyrolysis oil admixtures the regenerator temperature increases and cooling was necessary to reach the required riser temperature. The VGO experiments showed a decrease in temperature from riser bottom to the top. Experiments with pyrolysis oil admixtures had a different trend due to relatively low catalyst temperature in the bottom part. This led to higher reaction temperature in the upper part of the riser thus promoting secondary cracking. Higher C/O-ratios for experiments with pyrolysis oil addition also supported secondary cracking. These two process parameters may have enhanced gas formation.

For admixtures with more than 20 m% pyrolysis oil no stable operation point could be found. The feed tended to strong coking in the feed inlet area after a few minutes of operation. As a result the riser clogged and circulation collapsed.

One of the big advantages of the presented technology is the possibility of co-processing in existing petroleum refineries. The large scale of these facilities leads to high efficiency in the conversion and product upgrading process. Additionally, considerable amounts of propene and ethene are formed which can be used to produce polymers out of renewable sources.

ACKNOWLEDGEMENT

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