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Upgrading of heat carrier oil derived from liquid-phase pyrolysis via fluid catalytic cracking

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ABSTRACT

Second generation biofuel technologies are well investigated to extend the amount of sustainable biofuels. One of the most important criterions for biofuels is their profitability. The bioCRACK process is a new and innovative biomass-to-liquid concept to produce advanced biofuels by liquid-phase pyrolysis. A refinery integrated pilot plant was built up at the OMV refinery in Schwechat (Austria) to provide data for up-scaling. The objective of this publication was to test the suitability of different processed heat carrier oils derived from the bioCRACK process as feedstock for the FCC process. Vacuum gas oil – a typical feedstock for fluid catalytic cracking – was used as heat carrier oil. Different case studies were evaluated, whereas spruce wood and wheat straw were used as feedstock for pyrolysis. All experiments were conducted in a fully continuous small scale pilot plant with internally circulating fluidized bed design. In general, the obtained results show a high conversion efficiency for all performed case studies. Thereby the yield of coke is increased a little. The investigation confirmed that the total fuel yield can be improved even more by additional hydrotreatment. It turned out that the use of a pre-hydrotreated vacuum gas oil for pyrolysis leads to the highest conversion level.

1. Introduction

Currently fossil fuels are the most important global energy carriers [1]. They are predominantly used for the production of heat, fuels, electricity and chemicals. It is certain, however, that existing reserves are finite. In addition to that fact there are yet unknown risks about the rising concentration of greenhouse gases in the atmosphere and the resulting climatic change [2]. As a result research focus is placed on technologies which substitute fossil energy carriers by renewable sources to reduce the amount of greenhouse gases in the atmosphere. In 2009 the European Union committed itself to the 20–20–20 targets [3]. These targets include a 20% reduction in EU greenhouse gas emissions from 1990 levels. Technologies to produce heat and electricity from renewable sources are already well-developed and successfully used. Greater difficulties in development arise from production of liquid transportation fuels and chemicals. So far, especially first generation biofuels made from food crops are used to replace a certain amount of emissions in the transportation sector [4]. But actually first generation biofuels are controversially discussed because of the so-called food vs. fuel dilemma [5]. Efforts are therefore made to produce second generation fuels – also called advanced biofuels – manufactured from non-food feedstocks. The IEA estimates that advanced biofuels will gain market share after 2020, reaching 20% of biofuels supply in 2035 [6].

The bioCRACK process constitutes a new approach in the research field of advanced biofuels. It is a new biomass-to-liquid concept to produce advanced biofuels via liquid-phase pyrolysis [7–11]. Therefore lignocellulosic biomass is pyrolyzed with a heat carrier oil. BDI — BioEnergy International AG in cooperation with OMV AG tested a fully integrated pilot plant located at the refinery in Schwechat (Austria). The integration of the bioCRACK process enables sharing of already existing refinery facilities and utilities which can be used for upgrading formed reaction products. Vacuum gas oil (VGO) — a typical feedstock for fluid catalytic cracking (FCC) — is used as heat carrier oil. Thereby a certain amount of bio-carbon is transferred into the heat carrier oil during pyrolysis. Due to the low oxygen content of the heat carrier oil it can be converted as usual by means of fluid catalytic cracking.

Fluid catalytic cracking is one of the most important refinery processes to convert heavy oil fractions into more valuable gaseous olefins and high-octane gasoline. Nearly every refinery worldwide operates an FCC plant. Therefore, it is entirely reasonable to use this facility for upgrading all kinds of bio-feedstocks. Through co-processing with VGO, production of biofuels can be performed at lowest possible expenditure. At Vienna University of Technology, Reichhold and Hofbauer designed and constructed a small scale pilot plant with internally circulating fluidized

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bed (CFB) design [12]. The pilot plant is working as a continuous reaction and regeneration system, which allows a high comparability to large scale plants. Previous investigations showed that pure vegetable oils are suitable feedstocks for the FCC process to produce first generation biofuels [13]. In current studies upgrading of residue from a co-pyrolysis with VGO and lignocellulosic biomass via FCC is examined to produce second generation fuels [14]. However, due to the high oxygen content of pyrolysis oils in general there is a high tendency to coke formation. Thus pyrolysis oils have to be upgraded first by hydrotreatment and co-processed in smaller amounts together with VGO [15].

The objective of this publication was to test the suitability of different processed heat carrier oils derived from the bioCRACK process as feedstock for the FCC process. Therefore spruce wood and wheat straw were used as feedstock for liquid-phase pyrolysis. Four different case studies were evaluated. In each case study the heat carrier oil before and after performed pyrolysis was processed in the FCC pilot plant to investigate the change in catalytic conversion. Additionally, experiments with hydrotreatment were conducted for spruce wood to improve the conversion efficiency. The influence on the FCC yields and the crack gas composition of the bioCRACK process were observed and compared. Furthermore conversion efficiency and tendency to formation of coke of all investigated case studies were analyzed.

2. Experimental

2.1. FCC pilot plant

All experiments were conducted in a fully continuous FCC pilot plant with an internally circulating fluidized bed system at Vienna University of Technology. Generally, a continuous FCC plant consists of a reaction zone (usually designated as a riser), where the cracking reactions take place and a regeneration zone, where the spent catalyst is regenerated. Commercial FCC units are designed as externally circulating fluidized bed systems – reaction and regeneration unit are arranged separately. The FCC pilot plant shown in Fig. 1 is constructed as an internally circulating fluidized bed system, which means that the riser is concentrically arranged in the regenerator. The major advantages of this system can be found in the compact design and the improved heat-coupling between reaction and regeneration zone.

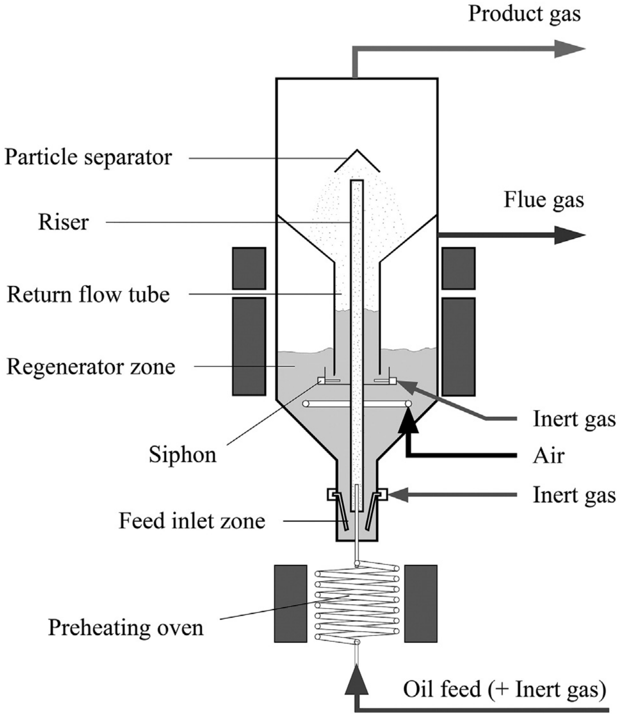

Fig. 1. FCC pilot plant scheme.

The feed is preheated in a tubular oven slightly below the initial boiling point (approximately 260–320 °C) and enters the pilot plant through the feed inlet pipe at the bottom of the riser. At this point the feed comes in contact with the hot catalyst and evaporates instantaneously. Now heterogeneous catalysis starts and the feed is cracked into smaller molecules. Due to the large increase in volume a strong upwards expansion occurs, which transports the catalyst pneumatically to the end of the riser. The mean riser residence time of the formed product gas is less than a second. During this period the catalyst is slightly deactivated because of the coke formed on its surface. At the particle separator product gas and catalyst are separated. Since the cross sectional area of the upper part is much bigger in comparison to the riser, fluidization velocity of the catalyst particles decreases below transportation velocity. As a result, the catalyst particles fall down to the return flow tube. A nitrogen fluidized siphon transfers the catalyst particles further on into the regenerator. There the coke deposited on the catalyst surface is burned with air in a bubbling fluidized bed. The heat generated during combustion is required for the endothermic cracking reactions and is transported from the regenerator into the riser by the hot catalyst particles as well as by direct heat transfer. The flue gas leaves the regenerator sideways; its composition is determined by a gas analyzer for calculation of the coke yield. Finally, the regenerated catalyst moves downwards to the feed inlet zone where the cycle starts again.

The formed product gas leaves the pilot plant at the top through a heated product pipe and is then burned in a flare. For analysis purposes a partial current is extracted by a diaphragm pump before the product gas enters the flare. The product gas to be analyzed is condensed by three intensive coolers and a droplet separator. The remaining gaseous hydrocarbons are guided through a gas-sampling tube and further on to a gas meter. In the end they are traced back to the flare. Both gaseous and liquid samples are analyzed by means of gas chromatography.

The siphon and the feed inlet zone are fluidized by inert gas (nitrogen) adequately to act as a gas barrier between the regeneration and the reaction zone. These devices also allow a homogenous and continuous catalyst circulation inside the pilot plant. The fluidization gas inside the siphon assures stripping of adsorbed hydrocarbons and transfers the catalyst into the regeneration zone. The fluidization gas at the feed inlet zone assures stripping of residual oxygen coming from the regenerator and provides stable and even catalyst transportation into the riser. The basic dimensions and characteristics of the FCC pilot plant are depicted in Table 1.

2.2. Applied feedstock

All investigated heat carrier oils for the FCC unit originate from the bioCRACK process mentioned above. Due to the use of a heavy oil fraction as heat carrier oil for liquid-phase pyrolysis, it appears to be

Table 1
Basic dimensions and characteristics 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 particle size range	20–200 μm
Riser temperature	500–600 °C
Regenerator temperature	610–650 °C
Feed flow	1–3 kg/h
Riser residence time	ca. 0.9 s
Pressure	Ambient
Fluidization bottom	1.5 Nl/min
Fluidization siphon	8 Nl/min
Fluidization regenerator	29 Nl/min
Flue gas oxygen	1–2 vol.%