

# The BioCRACK Process - A Refinery Integrated Biomass-to-Liquid Concept to Produce Diesel from Biogenic Feedstock

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Second generation biofuels, especially fuels from lignocellulose biomass, which are manufactured from non-food feedstock play a key role to reduce greenhouse gas emissions and the dependency on fossil oil. The bioCRACK process represents a new biomass-to-liquid concept to generate advanced biofuel by liquid-phase pyrolysis. As liquid heat carrier vacuum gas oil (VGO), an intermediate heavy oil product from the vacuum distillation, is used.

Since autumn 2012 a fully integrated pilot plant at the refinery in Schwechat/Austria with a nominal biomass capacity of 100 kg/h is in continuous operation and generates data for up-scaling the technology to an industrial scale.

This paper reports the results of the continuous operation. The influence of various reaction parameters, such as the reaction temperature, on yield and composition of the reaction products were investigated. As expected from previous results with a semi batch lab-scale reactor, within the selected range of temperature (350 °C to 400 °C), elevated temperature leads to decreasing amount of biochar and rising liquefaction. Based on the results could be shown that 10 to 20 % of the biogenic carbon can be transferred directly into raw fuels with the bioCRACK concept. Additionally 11 to 18 % of the bio-carbon merges into the remaining heat carrier.

## 1. Introduction

Transportation represents about 27 % of the total primary energy demand and is almost exclusively fuelled by mineral oil. The share may increase by 38 % from 2010 to 2035 (IEA, 2012). Therefore, and not least because of the fact that the global transportation sector is responsible for 22 % of the global greenhouse gas emissions (Olivier et al., 2012), the transport sector is challenged to play a key role to achieve the global targets relating to greenhouse gas emissions. The European Union has the ambitious aim to achieve at least ten percent of renewable energy share in the transport fuel sector until the year 2020. Furthermore the greenhouse gas emissions should be reduced by 20 % until 2020 (EU, 2009).

A few main routes can be distinguished to produce biofuels: extraction of vegetable oils, fermentation of sugars to alcohol, gasification and chemical synthesis and direct liquefaction (Hamelinck and Faaij, 2006). Due to the characteristic of their manufacture, commercially available biofuels employ almost uniquely food crops as their feedstock - predominantly sugar cane and sugar-beet, corn and oil seeds (Sorda et al., 2010). In comparison, second generation biofuels, also called advanced biofuels, are manufactured from non-food feedstock. The IEA (2011) assumes that especially the demand of advanced biodiesel is increasing in the foreseeable future. For this reason, intensive research and developing activities for advanced biofuel technologies are required to achieve the global targets.

BDI-BioEnergy International AG and OMV have been jointly involved in the bioCRACK pilot plant project to develop a new biomass-to-liquid concept to generate second generation biofuel. The process bases on the liquid phase pyrolysis (LPP) of lignocelluloses feedstock. In addition to fast pyrolysis and Fischer-Tropsch synthesis liquid phase pyrolysis is dedicated to form solid and liquid products. Mertlitz (2010) and

Schwaiger (2011) investigated the formation of liquid and solid products during liquid phase pyrolysis of wood with a semi-batch lab scale reactor. With rising reaction temperature the formation of biochar decreases, while formation of liquid CHO-products linearly correlates with the operation temperature. Schwaiger et al. (2012) reported additionally that the lignin frame in wood remains without substantial loss, while the major amount of carbohydrates is pyrolysed during liquid phase pyrolysis at  $T = 350\text{ }^{\circ}\text{C}$ . Building on the experiences with the semi-batch lab scale reactor a fully integrated pilot plant at the refinery in Schwechat/Austria with a biomass capacity of nominal 100 kg/h was established. This paper reports the results of the experimental tests performed on the continuous pilot-scale plant. The influence of various reaction parameters, such as the reaction temperature, on yield and composition of the reaction products was investigated.

## 2. Experimental

### 2.1 bioCRACK process

The bioCRACK concept is shown in Figure 1. To allocate high heat transfer and to avoid dust formation during the reaction, the pyrolysis process was carried out in liquid-phase. Feedstock for the experiments was lignocellulosic biomass (spruce wood and wheat straw). As liquid heat carrier vacuum gas oil (VGO), an intermediate heavy oil product from the vacuum distillation, which can be transformed into gasoline and diesel fuel by means of fluid catalytic cracking (FCC), is used. The biomass and the vacuum gas oil join the reaction by temperatures from  $350\text{ }^{\circ}\text{C}$  to  $400\text{ }^{\circ}\text{C}$ . Reaction products of the bioCRACK liquid-phase pyrolysis are condensable liquid products (pyrolysis oil, reaction water, raw fuel), non-condensable products and biochar as solid residue.

On account of the fact, that the bioCRACK process is based on the liquid phase pyrolysis (LPP) and uses as heat carrier a heavy oil fraction from the refinery it is obvious that the integration of the process in an already existing refinery is conducive. Figure 1 shows a feasible way of integration for the bioCRACK technology in a refinery. Apart from the using of the heavy oil fraction there are further synergies arising from the fact that the process will be integrated in an existing refinery. The already in the refinery existing utilities (steam, power, cooling water, nitrogen) are also required for the bioCRACK process. Moreover, the reaction products can be upgraded with the already existing facilities in the refinery. For example the raw fuel is upgradeable via hydrogenation to diesel fuel with renewable content, according to the EN590 standard. Other refinery facilities like the FCC (Fluid Catalytic Cracker) can be used for upgrading the bioCRACK products as well.

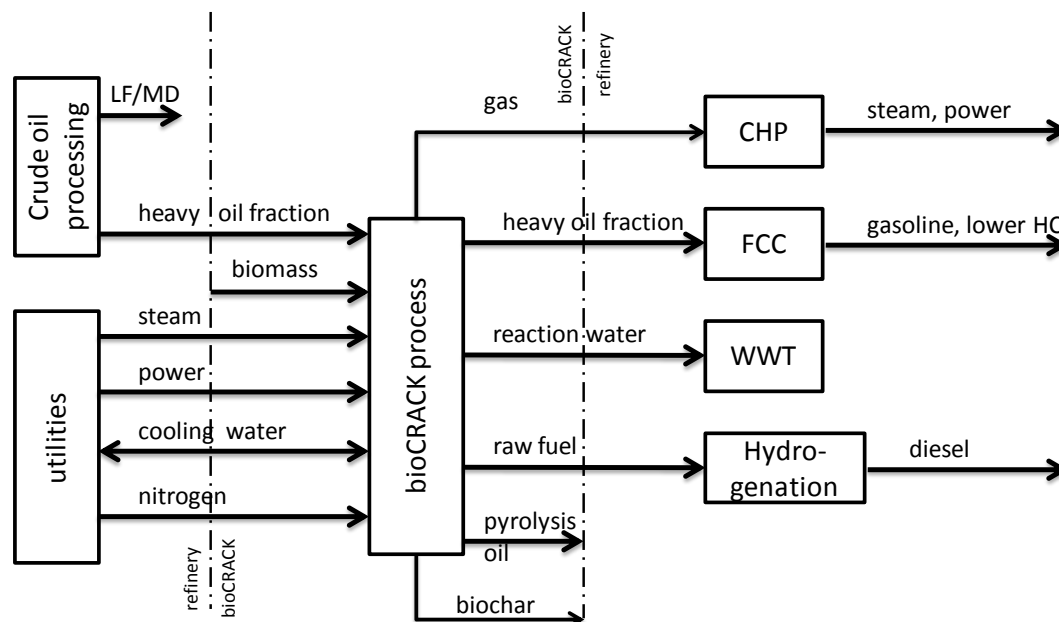


Figure 1: Possible integration of the bioCRACK process in a refinery

Table 1: Test parameter

Parameter		Range
Biomass-Feed	kg/h	60 - 100
Reaction Temperature	°C	350 - 400
VGO / Biomass ratio	-	3 - 6

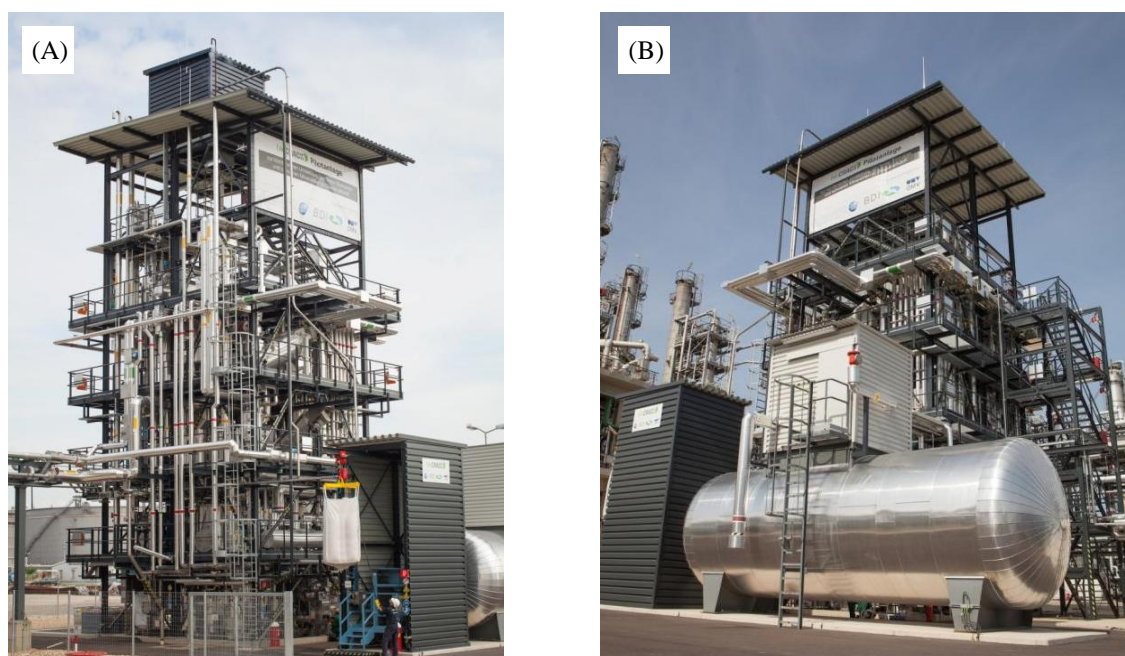


Figure 2: (A) Pilot plant at the refinery Schwechat/Austria, (B) Heat carrier oil vessel

## 2.2 Pilot plant and experimental procedure

The bioCRACK concept will be tested in a fully integrated pilot plant at the refinery Schwechat/Austria. Since autumn 2012 the pilot plant is under continuous operation for upscaling purposes to a demo plant. Figure 2 shows the bioCRACK plant. The nominal biomass capacity is 100 kg/h. The mass ratio varies between three to six parts of VGO to one part of biomass and the reaction temperature is altered between 350 °C and 400 °C. Table 1 shows an overview of the used test parameter.

## 3. Results

The influence of different test parameter (Table 1) on distribution and chemical composition of the reaction products were investigated. During liquid phase pyrolysis (LPP) the lignocellulosic biomass is transferred into hydrocarbons (mixed oil, carrier oil), liquid CHO-products, reaction water, biochar and gaseous products. Figure 3 shows the carbon balance of biogenic carbon, deduced from  $^{14}\text{C}$ -analysis, at 375 °C. In this case 16 % of the biomass were directly transferred into fuel fractions. In general, the experiments have shown that with the bioCRACK concept about 10 to 20 % of bio-carbon can converted directly into raw fuels. Additionally 11 to 18 % of the biogenic carbon merges into the remaining carrier. During the LPP of spruce at 375 °C, see Figure 3, 15 % of bio-carbon transfers into the remaining heat carrier (heat carrier oil - after treatment).

The used heat carrier oil - vacuum gas oil (VGO) - also degrades during the bioCRACK process into reaction products. The conversion of the carrier oil in relation to the carrier oil to biomass ratio shows Figure 4. Particularly the conversion into gasoil decreases with increasing VGO to biomass ratio. The total conversion rate of the VGO with carrier oil to biomass ratio of three is 20 %. While with increasing carrier oil to biomass ratio the conversion rate decreases. With a VGO to biomass ratio of about six the total conversion rate declined below 12 %.

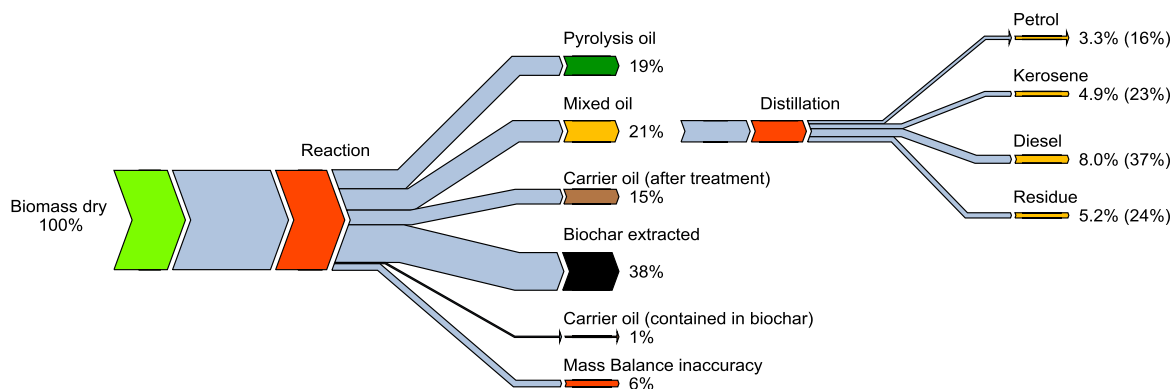


Figure 3: Carbon balance at  $T = 375\text{ }^{\circ}\text{C}$ , spruce wood

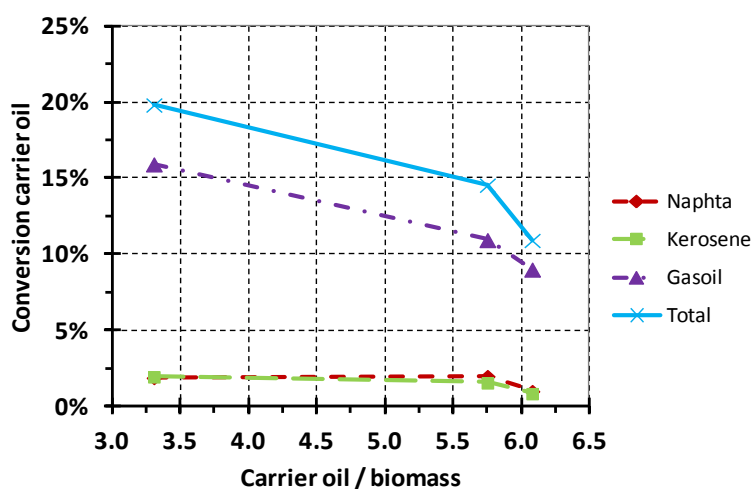


Figure 4: Conversion of the carrier oil

As expected from previous results with a semi batch lab-scale reactor (Mertlitz, 2010) and more recently (Schwaiger, 2011), within the selected range of temperature ( $350\text{ }^{\circ}\text{C}$  to  $400\text{ }^{\circ}\text{C}$ ), elevated temperature leads to decreasing amount of biochar and rising liquefaction as shown in Figure 5 and Table 2. At temperatures below  $385\text{ }^{\circ}\text{C}$  biochar is the dominant reaction product. The ratio of biochar formed during the liquid-phase pyrolysis decreases linearly, while the formation of liquid CHO-products and hydrocarbons increase with rising temperature.

Table 2: Distribution of the reaction products dependent on the reaction temperature

		350 °C	375 °C	390 °C
Hydrocarbons	[wt.%]	11	19	20
Liquid CHO-products	[wt.%]	18	20	23
Reaction water	[wt.%]	20	20	24
Biochar	[wt.%]	36	28	22

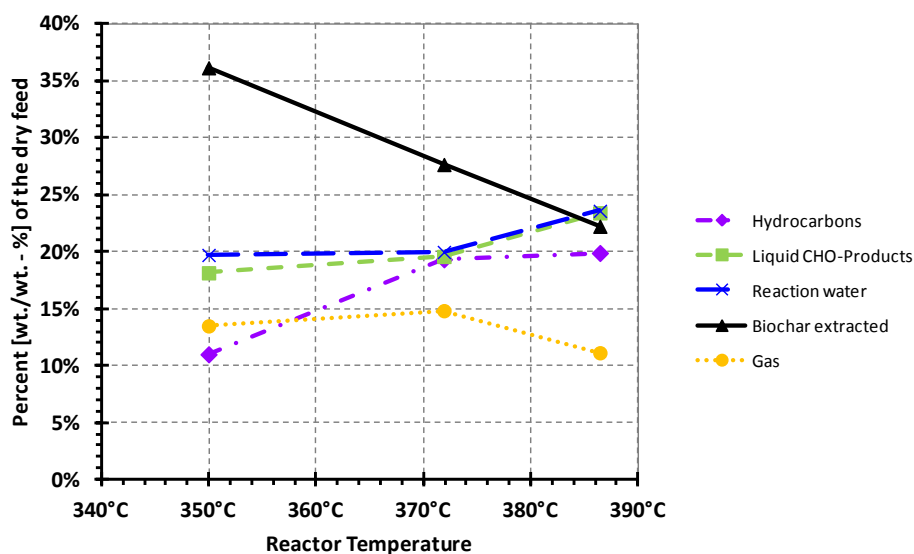


Figure 5: Effect of temperature on the mass conversion of spruce wood, 60 kg/h

The carbon balance of biogenic carbon dependent on the reaction temperature, illustrate in Figure 6, exhibits the same results. With increasing temperature the biochar yield sinks and the transfer of the biogenic carbon, deduced from  $^{14}\text{C}$ -analysis, into liquid fractions (pyrolysis oil, hydrocarbons - mixed oil and carrier oil) rises.

As already mentioned, bio-carbon is mainly converted into biochar during the liquid-phase pyrolysis (Figure 3). Table 3 shows the transfer of elements from lignocelluloses biomass to biochar during the bioCRACK process. Due to the elevated carbon content biochar is a considerable feedstock for direct liquefaction in order to produce biofuels (Feiner et al., 2013).

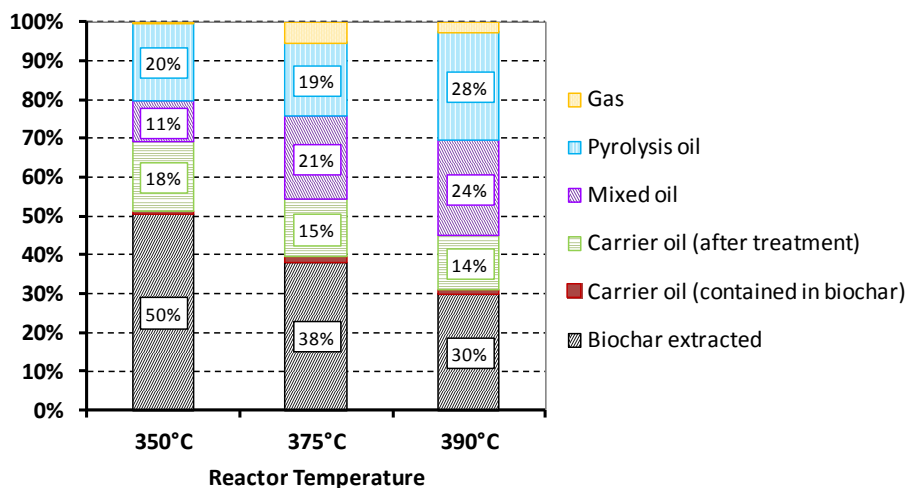


Figure 6: Effect of temperature on bio-carbon transfer of spruce wood, 60 kg/h

Table 3: Ultimate analysis of biomass and biochar

Compound		Biomass	Biochar
Carbon	[wt.%]	49.6	80.9
Hydrogen	[wt.%]	6.3	5.4
Nitrogen	[wt.%]	0.0	0.3
Rest (Oxygen + Ash)	[wt.%]	44.2	13.4

#### 4. Conclusion

Liquid-phase pyrolysis experiments are carried out in an innovative biomass-to-liquid pilot plant to generate advanced biogenic diesel. The results show, that the up-scaling from a semi batch lab-scale reactor to a pilot plant was successful. Comparable results were obtained under the various operation conditions. The bioCRACK process thus represents a new opportunity to manufacture advanced biofuel from lignocellulose biomass.

Further investigations will be conducted to optimize the bioCRACK concept and to generate data for up-scaling the technology to a demo plant.

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