Wood Derived Fast Pyrolysis Bio-liquids as Co-feed in a Fluid Catalytic Cracking Pilot Plant: Effect of Hydrotreatment on Process Performance and Gasoline Quality

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ABSTRACT: Co-feeding biogenic feeds in fluid catalytic cracking (FCC) units benefits from exploiting existing refinery assets to produce biogenic fuels. It is the most cost-effective way to comply with step-by-step increasing the target of renewable energy in road and rail transport of the European Union. Fast pyrolysis bio-liquids derived from wood offer a unique opportunity to reach those targets without having to address the typical food vs fuel debate. In the present work bio-liquids derived from pine wood in different stages of treatment were tested for their processability in a pilot scale fluid catalytic cracking plant at 550 °C. Specific focus is on the quality of the derived gasoline fractions. All samples were co-fed with vacuum gas oil, a typical FCC feed. Relevant parameters to qualify the produced gasoline as blending component were analyzed. As main results, none of the parameters examined significantly affect the quality of the—now partially biogenic—gasolines, demonstrating the potentiality of the co-FCC process as a possible near future pathway to ensure high biofuel contents in commercially available fuels.

INTRODUCTION

To comply with the step-by-step increasing minimum target of the share of renewable energy within the final consumption of energy in the transport sector set by the European Union (EU), the commercialization of new biofuel production technology will be necessary. In 2019, 74 million tons of gasoline were consumed by the EU Member States,1 while the globally consumed amount of liquid fuels estimates 97.4 million barrels per day in April 2022.2 By 2030, the share of renewable energy must reach a minimum share of 14% in each Member State.3 The package of proposals called “Fit for 55: delivering the EU’s 2030 Climate Target on the way to climate neutrality” even states that a 90% reduction in overall transport emissions by 2050 is required to reach the goal of climate neutrality.3

The Project “WASTE2ROAD—Biofuels from Waste to Road Transport” funded by the European Framework Programme for Research and Innovation Horizon 2020, aims to establish cost-effective value chains from low-cost biogenic residues and waste fractions to biofuels. The objective is to reach overall biomass-to-fuel-carbon yields exceeding 45% while reducing greenhouse gases emissions by more than 80%. This may be done by using existing refinery technologies to allow a quick and easy implementation. The project partners cover the whole value chain from waste management to tests of the created biofuels.4

The fluid catalytic cracking (FCC) process plays a key role in integrated refinery as one of the primary conversion processes. FCC units convert high-boiling petroleum fractions into lighter products, which are usually products of higher value,5 such as gasoline and olefins. The influence of the reaction temperature6 and the used catalyst7 on the product spectrum and the deployable feeds make it a process with a high degree of tailorability.8

The co-feeding of biomass-derived oils9,10 such as vegetable oils,11 fatty acid methyl12 ester (FAME), or pyrolysis oil from biomass13−16 as well as the use of waste-derived pyrolysis oils17,18 in FCC units has generated a lot of attention in the scientific search for possibilities to provide fuels with smaller carbon footprints. Some of these alternative feeds are targets of the food vs fuel dilemma, whereas others use eucts currently declared as waste. The next step on the path of implementing this research in the industrial setting is to verify the usability of the produced FCC gasoline as a gasoline blending component.

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Materials and Methods. Bio-liquids. The bio-liquids were provided by Biomass Technology Group B. V. (Netherlands; BTG), and their properties are listed in Table 2. The utilized bio-liquid batches were taken between the different processing steps pinewood undergoes during its conversion to so-called stabilized deoxygenated pyrolysis oil. A schematic of the process is provided in Figure 1. Details to the different conditions of the applied hydrotreatments are listed in Table 1. The pinewood is processed via fast pyrolysis to pyrolysis oil (PO), which is hydrogenated at mild conditions to stabilized pyrolysis oil (SPO) over a dedicated Picula catalyst. The SPO is further hydrogenated under more extreme conditions using conventional catalysts to so-called stabilized deoxygenated pyrolysis oil (SDPO).

Vacuum Gas Oil and Catalyst. Both the hydrotreated vacuum gas oil (VGO) and the equilibrium catalyst were provided by the OMV Schwechat refinery. Hydrogenation of VGO aims to remove impurities, such as nitrogen and sulfur. In Table 2 different properties of the hydrogenated VGO provided by OMV are listed in comparison to the properties provided by BTG for the bio-liquids.

Table 1. Conditions of the Hydrotreatments

| Conditions       | Catalyst | Temp (°C) | Pressure (bar) |
|------------------|----------|-----------|---------------|
| Mild hydrogenation | Picula   | 80−250    | 200           |
| Severe hydrogenation | CoMo/NiMo | >300      | 200           |

Table 2. Comparison of the Properties from the Used Feeds

| Param          | Unit    | PO    | SPO   | SDPO  | VGO   |
|----------------|---------|-------|-------|-------|-------|
| Total sulfur   | mg/kg   | n.d.  | n.d.  | n.d.  | 291   |
| Total nitrogen | mg/kg   | n.d.  | n.d.  | n.d.  | 275   |
| Nickel         | mg/kg   | <1    | n.d.  | n.d.  | 2     |
| Vanadium       | mg/kg   | <1    | n.d.  | n.d.  | 2     |
| Carbon         | wt %    | 43.9  | 54.1  | 85.5  | n.d.  |
| Hydrogen       | wt %    | 7.9   | 9.3   | 10.4  | n.d.  |
| Water content  | wt %    | 20.5  | 8.9   | 0.5   | n.d.  |
| Acid no.       | mg of KOH/g | n.d. | 35.2  | 7.0   | n.d.  |
| pH             |         | n.d.  | 5.29  | 3.83  | n.d.  |
| Ash content    | wt %    | 0.01  | n.d.  | n.d.  | n.d.  |
| Conradson      | wt %    | 20.459| 10.780| 1.973 | 0.202 |
| Carbon residue |         | n.d.  | n.d.  | n.d.  | 23.8  |

“n.d., not determined.”

Compared to fresh catalyst, the use of equilibrium catalyst provides a proper simulation of industrial plant conditions within a pilot plant. The provided equilibrium catalyst consists of two commercially available zeolite catalysts designed to maximize the production of propylene, butanes, and butenes.

Pilot Plant. The FCC pilot plant, situated at the Institute of Chemical, Environmental and Bioscience Engineering (ICEBE) at Technical University Wien, was developed by Bielansky, based on a prototype designed by Reichhold. The continuously operating pilot plant is constructed as an internally circulating fluidized bed system, where the reactor section (riser) is located in the regenerator section. In Figure 2 a schematic of the pilot plant is depicted.

Figure 1. Schematic of the processing steps from pinewood to stabilized deoxygenated pyrolysis oil.

Figure 2. Schematic of the FCC pilot plant.

Feeds are pumped into a tubular oven to be preheated close to boiling temperature. This occurs via a feeding system that allows the use of two different pumps, enabling the co-feeding of two feeds, if these are not miscible. In the case of miscible feeds, one of the pumps can be bypassed. After the preheating, the feedstock is injected into the riser to come into contact with the hot catalyst. This leads to instant evaporation and thus an increase in volume by several orders of magnitude, creating an upward flow that transports the catalyst particles from the bottom of the plant through the riser top where they are separated from the product gas and fall down into a siphon. This siphon and the bottom section (so-called bottom) act as a gas barrier between the riser and the regenerator. The siphon also serves as a stripper that removes the remaining product gas from the catalyst particles. The product gas is transported to a flare or sampled to carry
Catalyst particles enter the regenerator through the siphon, where the coke deposited on the catalyst particles during the cracking process in the riser is combusted at a temperature of 610 °C. The combustion of coke ensures the regeneration of the catalyst and provides the thermal energy that is needed to facilitate the endothermic cracking reactions. The hot catalyst then passes through the cooler section where heat exchangers, operated with air or water, are applied to control the temperature of the catalyst that enters the bottom.

Bottom, siphon, and riser of the pilot plant are fluidized with nitrogen since the catalytic cracking reaction has to take place in the absence of oxygen, whereas cooler, regenerator, and free board sections of the pilot plant are fluidized with air to feed the oxygen required in the combustion reactions. Key data of the pilot plant are listed in Table 3.

### Table 3. Key Data of the FCC Pilot Plant

| Parameter              | Value     |
|------------------------|-----------|
| Total height           | 3.2 m     |
| Riser length           | 2.5 m     |
| Riser diameter         | 0.0215 m  |
| Regenerator diameter   | 0.33 m    |
| Regenerator temperature| 500–800 °C|
| Riser temperature      | 400–700 °C|
| Pressure               | Atmospheric|
| Catalyst mass          | 45–75 kg  |
| Feed rate              | 1.5–8 kg/h|
| Riser residence time   | ~1 s      |
| Catalytic circulation  | 0.5–5 kg/min|
| C/O ratio              | 10–50     |

During the sampling process, part of the product gas is directed thru a system of coolers (water and ethanol (−15 °C)) to condense all products that are liquid at room temperature. Afterward the gashouse phase passes through a gas collection tube and a gas meter. Each sample collection takes place over the course of 15 min. Throughout an experiment several samples are collected, which are analyzed multiple times.

The experiments were conducted at a feed temperature of 320 °C, a riser temperature of 550 °C and a feed rate of 2 kg/h, resulting in a C/O ratio between 23 and 27. The experimental ID’s and compositions are described in Table 4.

### Table 4. Experiment Parameters and ID’s

| ID | VGO content (wt %) | admixture | admixture content (wt %) |
|----|--------------------|-----------|--------------------------|
| PO | 95                 | PO        | 5                        |
| SPO| 95                 | SPO       | 5                        |
| SDPO| 95                | SDPO      | 5                        |
| VGO| 100                |           |                          |

**Analysis.** A so-called lump model is used to analyze the data. In this model, the products are categorized in different groups/lumps, which are characterized as a group, eliminating the need of characterizing every occurring component. The lump model is further detailed in Table 5.

Online analysis of oxygen, carbon monoxide, and carbon dioxide in the flue gas and the product gas was conducted using a unit that combines an infrared gas analyzer and a paramagnetic oxygen analyzer (NGA 2000 MLT 3, Emerson). The data of the flue gas measurements were used to calculate the coke production.

Furthermore, the concentrations of hydrocarbons and nitrogen in the product gas were analyzed in a gas chromatograph (GC-17A, Shimadzu). The GC utilizes two columns (Varian CP-Al2O3/Na2SO4; CP CarboPLOT P7), an FID, and a TCD.

### Table 5. Details of the Employed Lump Model and Used Analysis Methods

| Fraction  | Product Group   | Boiling Range, Composition | Analysis Method         |
|-----------|-----------------|----------------------------|-------------------------|
| Gaseous   | Carbon oxides   | CO, CO2                    | nondispersive infrared spectroscopy, gas chromatography |
| Hydrocarbon gas   |                 | C1-C4                      |                         |
| Liquid    | Gasoline        | <210 °C                    | simulated distillation, further measurements |
| Light cycle oil residue |     | 210–320 °C                  | simulated distillation |
| Water     | H2O + dissolved substances |                   | gravimetric             |
| Solid     | Coke            | Burned-off substances      | flue gas composition    |

### RESULTS AND DISCUSSION

The three different provided bio-liquids were all processable in the FCC pilot plant as co-feed with VGO in admixture of 95 wt % VGO and 5 wt % bio-liquid. The typical duration of continuous feeding in the course of an experiment with stable conditions is 2.5 h. This duration could not be reached with the experiment with 5 wt % PO, which was slightly unstable. However, this circumstance does not speak against the use of PO as a co-feed in an FCC unit. Pinho et al. elaborates why certain operational instabilities are inherent to small-scale units and can be avoided in commercial FCC units through structural measures, such as supplying oxygenated feeds via a feed line that is kept below 50 °C.

**FCC Product.** Figure 3 is a depiction of the values listed in Table 6 for the different lumps, with the exception of the lumps carbon oxides and water due to their small values.

The data show that a higher grade of treatment of the bio-liquid is accompanied by a decrease in gas production and a rise in gasoline production. The conversion is defined by the weight percentage of products (here the sum of gas and gasoline) based on the feed used and slightly decreases with the treatment grade of the bio-liquid. This is due to the fact that not only the gasoline lump increases with severity but also the LCO lump, which, in this work, is not taken into account as a product since it is partially cycled back into the process in the simulated plant. Overall, the addition of bio-liquid thus leads to a minor decrease of conversion in comparison to the use of pure VGO (~1–1.5 wt %) and also to an increase of the produced amount of coke (~1 wt %). Partially this is due to the lower amounts of moles of carbon that is fed into the reactor system.

The produced amount of water (Table 6) is 0.9 wt % for PO and 0.4 wt % for SPO. SDPO and VGO did not produce water.
Figure 3. Product yields for catalytic cracking.

Table 6. Feed Based Results of the Lump Model for the Different Experiments

|                           | gas  (wt %) | gasoline (wt %) | LCO  (wt %) | residue (wt %) | coke (wt %) | carbon oxides (wt %) | water (wt %) | conversion (wt %) |
|---------------------------|-------------|-----------------|-------------|----------------|-------------|-----------------------|--------------|-------------------|
| PO                        | 47.9        | 36.3            | 5.0         | 3.7            | 5.7         | 0.6                   | 0.9          | 84.2              |
| SPO                       | 45.4        | 38.6            | 5.7         | 3.9            | 5.6         | 0.5                   | 0.4          | 83.9              |
| SDPO                      | 42.0        | 41.5            | 6.8         | 3.9            | 5.6         | 0.3                   | 0.0          | 83.5              |
| VGO                       | 45.0        | 40.0            | 5.8         | 4.0            | 4.9         | 0.3                   | 0.0          | 85.0              |

Table 7. Measured Parameters of the Gasoline Samples with Legal Requirements in ASTM D4814-16e or DIN EN 228:2017-08a

|                           | ASTM D4814-16e | DIN EN 228:2017-08 | PO gasoline | SPO gasoline | SDPO gasoline | VGO gasoline |
|---------------------------|----------------|--------------------|-------------|--------------|---------------|--------------|
| density (15 °C) sulfur    | kg/m³         |                   |             |              |               |              |
|                            | Min | Max | Min | Max | Min | Max | Min | Max | Min | Max | Min | Max | Min | Max |
| Methanol                  | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| Ethanol                   | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| Benzene                   | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| total Aromats             | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| total Olefins             | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| Total oxygen              | wt% |       |     |     |     |     |     |     |     |     |     |     |     |     |
| Final boiling point       | °C |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Reid Vapor Pressure       | kPa |      |     |     |     |     |     |     |     |     |     |     |     |     |

“Checkmark means the parameter has to be measured but there is no value limitation; the values marked with an asterisk (*) were first published by Büchele et al.27”
The collected water in the product is the sum of water present in the feed and water formed by the cracking reactions. Due to deoxygenation occurring during the cracking process not only in the form of dehydration but also as decarbonylation and decarboxylation, higher amounts of carbon oxides are seen in the experiments PO and SPO in comparison to SDPO and VGO.

**Gasoline Lump.** Table 7 shows the measured parameters of the gasoline samples that have set legal requirements in the standards ASTM D4814-16e or DIN EN 228:2017-08 or both. The checkmark symbol means the parameter has to be measured but there is no value limitation. The values marked with an asterisk (*) were first published by Büchel et al.

The values from Pb and the total of olefins are below the set maximum values. The content of oxygenated compounds such as alcohols and ethers of all samples lie below 0.1 wt %. The lack of oxygenated components is due to the deoxygenation occurring during the cracking process. For Mn the value is below 2.0 mg/L, which is stated as maximum value in DIN EN 228:2017-08, but the limit of detection of the used analysis method is above the maximum value of 0.25 mg/L in ASTM D4814-16e.

The sulfur content of all samples is below the maximum value of 0.0080 wt % mentioned in ASTM D4814-16e, but above 10 mg/kg mentioned in DIN EN 228:2017-08. Sulfur content in FCC gasoline is strongly related to the sulfur content in the used feed. Between 2 and 20% of the initial sulfur end up in the FCC gasoline, and the content can be as high as 3000 mg/kg for gasoline from unhydrogenated VGO.

The values for density (at 15 °C) and benzene and total aromatic content for all samples are above the maximum values defined in DIN EN 228:2017-08 (no values are stated in ASTM D4814-16e). Only the benzene value is slightly higher for the bio-liquid admixtures than for the pure VGO sample. The VGO gasoline samples have the highest values for density (15 °C) and total aromatic content. The vapor pressure of all gasoline samples is below the possible range between different fuel classes mentioned in the standards. The gasoline derived from PO has the lowest vapor pressure with 30 kPa, while VGO gasoline exhibits the highest vapor pressure with 36 kPa. All samples have a higher final boiling point than mentioned in the standards, but that is likely due to the distillation apparatus used in the present study, allowing higher-boiling compounds to be carried along. The utilized fractionating column between round-bottom flask and Liebig condenser was a 150 mm Vigreux column.

Since VGO gasoline is a gasoline blending component and the benzene value is only 0.2 wt % higher for the gasoline samples of the bio-liquid experiments, it can be concluded that the gasoline of all bio-liquid experiments can be used as gasoline blending component if the Mn value is low enough for ASTM D4814-16e. Higher sulfur values do not lead to exceeding the maximum sulfur content in the finished gasoline blend, since 80−95 wt % of the total sulfur content of the blend stems from FCC gasoline, whereas FCC gasoline only makes up around 20−40% of the blend. Thus the lower vapor pressure also does not pose a problem to reach the intended values in the blend.

Table 8 shows the measured parameters of the gasoline sample which must be measured according to ASTM D4814-16e or DIN EN 228:2017-08 but have no indication of maximum or minimum values.

| Parameter                  | ASTM D4814-16e | DIN EN 228:2017-08 | PO gasoline | SPO gasoline | SDPO gasoline | VGO gasoline |
|----------------------------|----------------|--------------------|-------------|--------------|---------------|--------------|
| Propane (v%)               | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| n-Butane (v%)              | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| n-Pentane (v%)             | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Toluene (wt%)              | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| C8 aromatic content (wt%)  | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| C9 aromatic content (wt%)  | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| C10 aromatic content (wt%) | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Polynaphthenes (wt%)       | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum Naphthenes (wt%)       | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum olef. Naphthenes (wt%) | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum i Olefins (wt%)        | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum n Olefins (wt%)        | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum i Paraffins (wt%)      | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Sum n Paraffins (wt%)      | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| Fe (mg/kg)                 | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| MTBE (wt%)                 | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| ETBE (wt%)                 | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| TAME (wt%)                 | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| t-Butanol (wt%)            | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |
| free water (mL/L)          | ✓              | ✓                  | ✓           | ✓            | ✓             | ✓            |

“Checkmarks mean the parameter has to be measured according to this standard; the values marked with as asterisk (*) were first published by Büchel et al.”

The collected water in the product is the sum of water present in the feed and water formed by the cracking reactions. Due to deoxygenation occurring during the cracking process not only in the form of dehydration but also as decarbonylation and decarboxylation, higher amounts of carbon oxides are seen in the experiments PO and SPO in comparison to SDPO and VGO.
Büchele et al.27 The detailed breakdown for naphthenes, olefins, and paraffins is available in the Supporting Information.

As listed in Table 7 the total aromatic content varies from 57.3 wt % (PO gasoline) to 63.8 wt % (VGO gasoline), with higher concentration of aromatics according to the treatment grade of the used bio-liquid. The main reason is the difference of the C8 and C9 aromatic contents (Table 8) between the PO gasoline and the VGO gasoline samples, which are both around 2.5 wt %, while differences between the other gasoline samples and VGO gasoline were lower.

The isopentane concentration of the gasoline increases with the treatment grade of the bio-liquid (3.9−4.7 wt %) and is higher than the pure VGO sample (3.7 wt %). The n-pentane concentration is also higher for the bio-liquid gasoline samples than for the pure VGO gasoline sample, but here the concentration decreases with the treatment grade of the bio-liquid.

The sum of olefinic naphthenes shows a big difference between PO gasoline (4.5 wt %), SPO gasoline (3.2 wt %), and VGO gasoline (2.7 wt %). SDPO gasoline has the lowest concentration with 2.4 wt %. The main differences are the concentrations of the C8, C7, and C6 olefinic naphthenes.

The sum of iso-olefins and the sum of n-olefins also show the same tendencies as the sum of olefinic naphthenes with the exception that the VGO gasoline sample has the lowest value and not the SDPO gasoline sample. The concentrations of iso-olefins are 7.8 wt % for PO gasoline, 6.2 wt % for SPO gasoline, 5.4 wt % for SDPO gasoline, and 5.1 wt % for VGO gasoline. The main reason for the difference in the iso-olefin concentration are the iso- C6 and iso-C5 olefinic compounds. The concentrations of n-olefins are 2.5 wt % for PO gasoline, 2.0 wt % for SPO gasoline, 1.8 wt % for SDPO gasoline, and 1.6 wt % for VGO gasoline. The main reason for the difference in the n-olefin concentrations are the n-C5 and n-C4 olefinic compounds. The reduction of olefinic products with the severity of the hydrotreatment matches the findings of Fogassy et al.15 and Schuurman et al.32 and is caused by the consumption of hydrogen that is necessary for the dehydroxylation of the oxygenated components.

Table 9 shows the measured parameters of the gasoline samples that are not mentioned in ASTM D4814-16e or DIN EN 228:2017-08. The values marked with an asterisk (*) were first published by Büchele et al.27.

The amount of dissolved water in the gasoline sample is the lowest for the VGO gasoline (101 mg/kg) and the highest for the SDPO gasoline (184 mg/kg). The nitrogen concentrations of the gasoline samples are 2.3 mg/kg for VGO gasoline, 6.4 mg/kg for PO gasoline, 7.5 mg/kg for SDPO gasoline, and 11.1 mg/kg. The carbon and hydrogen contents only vary between 0.3 wt % points. All of the additionally measured element concentrations are below the detection limit of the respective methods used.

#### CONCLUSION

The higher grade of treatment of bio-liquid is accompanied by a decrease in gas production and a rise in gasoline production during the FCC process. Overall, the addition of bio-liquid leads to a minor decrease of conversion, which is the weight percentage of product (gas and gasoline) based on the feed used, in comparison to the use of pure VGO (~1−1.5 wt %) and to an increase of the amount of coke (~1 wt %) produced.

Since FCC gasoline from VGO is a currently used gasoline blending component, it can be concluded that the gasoline of all bio-liquid experiments can be used as a gasoline blending component if the Mn value is low enough for ASTM D4814-16e, the higher sulfur values do not lead to exceeding the maximum value of sulfur in the finished gasoline blend, and the lower vapor pressure does not pose a problem to reach the intended values in the blend.

Not all key parameters of gasoline could be checked due to the amount of gasoline samples available. However, it shows the potentiality of the fluid catalytic cracking process as a possible refinement method for bio-liquids to enable higher biofuel content in commercially available fuel.

#### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01736.

Detailed breakdown of the paraffins, olefins, and naphthenes present in the gasoline samples (Table S1) (PDF)

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**Table 9. Measured Parameters of the Gasoline Samples That Are Not Mentioned in ASTM D4814-16e or DIN EN 228:2017-08**

| Parameter | PO | SPO | SDPO | VGO |
|-----------|----|-----|------|-----|
| initial boiling point°C | –5.2 | –5.9 | –5.4 | –8.6 |
| dissolved water mg/kg | 125* | 184* | 125* | 101* |
| nitrogen mg/kg | 6.4 | 11.1* | 7.5* | 2.3* |
| hydrogen wt % | 12 | 11.8 | 11.9 | 11.8 |
| carbon wt % | 87 | 87.2 | 87.1 | 87.3 |
| Al mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Ca mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Cr mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| K mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Mo mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Na mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Ni mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Si mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| V mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Zn mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Hg mg/kg | <0.003 | <0.003 | <0.003 | <0.003 |
| Ag mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Cd mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Cu mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Mg mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| Sn mg/kg | <1.00 | <1.00 | <1.00 | <1.00 |
| As μg/kg | <10.0 | <10.0 | <10.0 | <10.0 |
| sum of halogens (Cl, Br) μg/kg | <1 | <1 | <1 | <1 |

“The values marked with an asterisk (*) were first published by Büchele et al.27.”
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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Fuels consumption still affected by COVID-19 in 2021. Eurostat, July 4, 2022. https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20220407-1.
(2) Short-Term Energy Outlook. Independent Statistics & Analysis, U.S. Energy Information Administration (eia), July 12, 2022. https://www.eia.gov/outlooks/steo/report/global_oil.php (accessed May 12, 2022).
(3) Commission to the European Parliament; The Council; The European Economic and Social Committee; The Committee of the Regions “Fit for 55”: Delivering the EU’s 2050 Climate Target on the Way to Climate Neutrality. European Economic and Social Committee website, February 23, 2022; p 15. https://www.eesc.europa.eu/en/our-work/opinions-information-reports/opinions/fit-55-delivering-eus-2050-climate-target-way-climate-neutrality
(4) WASTE2ROAD. https://www.sintef.no/projectweb/waste2road (accessed May 12, 2022).
(5) Sadeghbeigi, R. Fluid Catalytic Cracking Handbook: An Expert Guid to the Practical Operation, Desing, and Optimization of FCC Units, 3rd ed.; Elsevier Science & Technology, 2012.
(6) AfsharEbrahimi, A.; Tarighi, S. The Influence of Temperature and Catalyst Additives on Catalytic Cracking of a Heavy Fuel Oil. Pet. Sci. Technol. 2015, 33 (4), 415−421.
(7) Büchele, M.; Lutz, H.; Kraus, F.; Reichhold, A. Catalyst Testing in a Continuously Operated Fluid Catalytic Cracking Pilot Plant. Proceedings of the 16th Minisymposium Verfahrenstechnik and 7th Partikelforum, TU Wien, Sep. 21−22, 2020; Association chemical-engineering.at, Verein zur Unterstützung der Verfahrenstechnikausbildung in Österreich.Vienna 2020.
(8) Passamonti, F. J.; de la Puente, G.; Sedran, U. Laboratory Evaluation of FCC Commercial Catalysts: Analysis of Products of Industrial Importance. Catal. Today 2008, 133−135, 314−318.
(9) Weinert, A. Katalytisches Cracken Alternativer Einsatzstoffe Aus Erneuerbaren Ressourcen. Diploma Thesis, Technische Universität Wien, Wien, Austria, 2009.
(10) Al-Sabawi, M.; Chen, J.; Ng, S. Fluid Catalytic Cracking of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review. Energy Fuels 2012, 26 (9), 5355−5372.
(11) Fimberger, J.; Swoboda, M.; Reichhold, A. Thermal Cracking of Canola Oil in a Continuously Operating Pilot Plant. Powder Technol. 2017, 316, 535−541.
(12) Weinert, A.; Bielansky, P.; Reichhold, A. Upgrading Biodiesel into Oxygen-Free Gasoline: New Applications for the FCC-Process. APCBEE Proc. 2012, I, 147−152.
(13) Eschenbacher, A.; Myrstad, T.; Bech, N.; Duus, J.O.; Li, C.; Jensen, P. A.; Henriksen, U. B.; Ahrenfeldt, J.; Mentzel, U. V.; Jensen, A. D. Co-Processing of Wood and Wheat Straw Derived Pyrolysis Oils with FCC Feed—Product Distribution and Effect of Deoxygenation. Fuel 2020, 260, 116312.
(14) Thegarid, N.; Fogassy, G.; Schuurman, Y.; Mirodatos, C.; Stefanidis, S.; Illopopoulou, E. F.; Kalogiani, K.; Lappas, A. A. Second-Generation Biofuels by Co-Processing Catalytic Pyrolysis Oil in FCC Units. Adv. Catal. B 2014, 145, 161−166.
(15) Fogassy, G.; Thegarid, N.; Toussaint, G.; van Veen, A. C.; Schuurman, Y.; Mirodatos, C. Biomass Derived Feedstock Co-Processing with Vacuum Gas Oil for Second-Generation Fuel Production in FCC Units. Appl. Catal. B Environ. 2010, 96 (3−4), 476−485.
(16) de Miguel Mercader, F.; Groeneveld, M. J.; Kersten, S. R.A.; Way, N. W.J.; Schaverien, C. J.; Hogendoorn, J. A. Production of Advanced Biofuels: Co-Processing of Upgraded Pyrolysis Oil in Standard Refinery Units. Appl. Catal. B Environ. 2010, 96 (1−2), 57−66.
(17) Knaus, F. Einsatz von Mixed Feedstocks Aus Rückstands- Und Recyclingfraktionen Im FCC-Prozess. Ph.D. Thesis, Technische Universität Wien, Wien, Austria, 2019.
(18) Swoboda, M.; Büchele, M.; Reichhold, A.; Hofer, W. Catalytic Conversion of Pyrolysis Oils Derived From Plastics in a Continuously Operated FCC Pilot Plant. Erdol.Erdgas.Kohle 2019135, 215−223.
(19) Gary, J. H.; Handwerk, G. E.; Kaiser, M. J. Petroleum Refining: Technology and Economics, 5th ed.; CRC Press, 2007.
(20) Ravichander, N.; Chiranjeevi, T.; Gokak, D. T.; Voolapalli, R. K.; Choudary, N. V. FCC Catalyst and Additive Evaluation—A Case Study. Catal. Today 2009, 141 (1−2), 115−119.
(21) Bielansky, P. Alternative Feedstocks in Fluid Catalytic Cracking, Ph.D. Thesis, Technische Universität Wien, Wien, Austria, 2012.
(22) Reichhold, A. Entwicklung von Reaktions/Regenerationssystemen Für Adsorptions/Desorptionsprozesse Und Für Katalytisches Cracken Auf Der Basis von Intern Zirkulierenden Wirbelschichten. Ph.D. Thesis, Technische Universität Wien, Wien, Austria, 1996.
(23) Pinho, A. de R.; de Almeida, M. B. B.; Mendes, F. L.; Casavechia, L. C.; Talmadge, M. S.; Kucher, C. M.; Chu, H. L. Fast Pyrolysis Oil from Pinewood Chips Co-Processing with Vacuum Gas Oil in an FCC Unit for Second Generation Fuel Production. Fuel 2017, 188, 462−473.
(24) Adjaye, J. D.; Bakshi, N. N. Catalytic Conversion of a Biomass-Derived Oil to Fuels and Chemicals I: Model Compound Studies and Reaction Pathways. Biomass Bioenergy 1995, 8 (3), 131−149.
(25) D20 Committee. Specification for Automotive Spark-Ignition Engine Fuel; ASTM International, 2017. DOI: 10.1520/D4814-16EE01 (accessed April 29, 2022).
(26) Technischen Komitee CEN/TC 19. Kraftstoffe—Unerwählte Ottokraftstoffe—Anforderungen und Prüfverfahren, Deutsche Fassung EN 228:2012+A1:2017; CEN-CENELEC-Management-Zentrum, 2014.
(27) Buechele, M.; Lutz, H.; Kraus, F.; Reichhold, A.; Venderbosch, R.; Vollhofer, W. Co-Feeding of Vacuum Gas Oil and Pinewood-Derived Hydrogenated Pyrolysis Oils in a Fluid Catalytic Cracking Pilot Plant to Generate Olefins and Gasoline [Version 1; Peer Review: 2 Approved]. Open Res. Eur. 2021, I, 143.
(28) Siddiqui, M. A.B.; Aitani, A. M. FCC Gasoline Sulfur Reduction by Additives: A Review. Pet. Sci. Technol. 2007, 25 (3), 299−313.
(29) Myrstad, T.; Seljestokken, B.; Engan, H.; Ryter, E. Effect of Nickel and Vanadium on Sulphur Reduction of FCC Naphtha. Appl. Catal. Gen. 2000, 192 (2), 299−305.
(30) Choi, J.-S.; Maugé, F.; Pichon, C.; Olivier-Fourcade, J.; Jumas, J.-C.; Petit-Clair, C.; Uzio, D. Alumina-Supported Cobalt-Molybdenum Sulfide Modified by Tin via Surface Organometallic Chemistry:
Application to the Simultaneous Hydrodesulfurization of Thiophenic Compounds and the Hydrogenation of Olefins. *Appl. Catal. Gen.* 2004, 267 (1–2), 203–216.

(31) Miller, J. T.; Reagan, W. J.; Kaduk, J. A.; Marshall, C. L.; Kropf, A. J. Selective Hydrodesulfurization of FCC Naphtha with Supported MoS2 Catalysts: The Role of Cobalt. *J. Catal.* 2000, 193 (1), 123–131.

(32) Schuurman, Y.; Fogassy, G.; Mirodatos, C. Tomorrow’s Biofuels. In *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*; Elsevier, 2013; pp 321–349. DOI: 10.1016/B978-0-444-56330-9.00010-3.