

Fuels from Reliable Bio-Based Refinery Intermediates – BioMates

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Abstract:

The overall aim of the project “BioMates” is to develop a conversion process for agricultural residues (cereal straw) or energy crops (miscanthus) into a liquid intermediate with reliable properties for the co-processing in existing petroleum refineries.

The process is divisible into two individual steps – ablative fast pyrolysis and mild hydrotreatment. Both biomass feedstocks were pyrolysed in a laboratory plant and optimal parameters leading to highest organic liquid yield were determined to be 540 °C at the hot surface, 50 bar hydraulic pressure and 80 rpm of rotational speed of the ablation plate. Different setups for condensation and catalytic vapour upgrade were tested and best results regarding highest organic yield with lowest water content could be achieved with a two-stage condensation operating at about 68 °C condensation temperature in the first stage. Here, a total yield of 41 wt.-% in (oxygenated) organic compounds could be achieved in the first stage condensate compared to only 36 wt.-% in the tarry phase of single stage condensation. Catalysts for direct upgrading of vapours were tested but found to be inappropriate in the current setup.

For mild hydrotreatment conventional sulphidized catalyst and newly developed non-sulphidized catalysts were tested. The new catalysts showed high initial reactivity but fast deactivation. Currently, the commercial catalyst with NiMo-system on Al₂O₃-support performed best, especially at 8 MPa hydrogen supply pressure and 360 °C operating temperature. Here, water content below 1 wt.-%, a density of organic product below 0.9 kg dm⁻³ and a lower heating value above 39 MJ kg⁻¹ was achieved.

Electrochemical compression and purification can supply hydrogen at necessary pressure and flow rate with acceptable energy demand and by that can replace mechanical compression on the supply side and pressure swing adsorption system in the recycle loop.

The project aims were fully achieved in TRL3-4 and will be demonstrated in TRL5 until the end of the project.

Keywords: ablative fast pyrolysis; bio-oil upgrade; hydrotreatment; electrochemical compression

Statement of Novelty

Petroleum refineries are nowadays looking for renewable feedstocks. Because biomass has solid nature, it must be converted to liquid state first. A possible conversion process is fast pyrolysis and due to unwanted properties of the liquids an upgrade process must be added. Presently research focusses on the direct co-feeding of raw pyrolysis condensates to FCC units (with a share below 5 %) or complete upgrade to finish fuel blendstock. The aim of BioMates project is to upgrade the pyrolysis liquid to a certain amount that it gains a quality able to be co-processed in a refinery to a significantly higher share. The whole process is to be developed from TRL3-4 to TRL5.

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1. Introduction

To date, road fuels are almost exclusively provided by blending fossil fuels from refineries with separately manufactured biofuels at the end of both processes to meet the required targets of bio-fuels content set out by rules from the European Union. There are some conventional refineries co-feeding vegetable oils in Europe, but since bio-oils' properties are incompatible with the conventional refinery processes, this is only possible at very low level. For future large-scale co-feeding of bio-based material into refineries (instead of blending finished fuels after the refinery processes), well-defined co-feed material would be essential. This is where "BioMates", a project funded by the European Union's research and innovation programme Horizon 2020, comes into play.

Having started in October 2016, the project aims at manufacturing intermediate products made from herbaceous non-food biomass, e.g. from agricultural residues. Such bio-based intermediates will be highly suitable for direct integration in a conventional oil refinery. The cost-effective and decentralised valorisation of agricultural residues and non-food crop biomass (like cereal straw and the perennial grass *Miscanthus x giganteus*) for the production of bio-based products is a key element of the project. The fossil-dominated refining sector could utilise a bio-based co-feed of reliable properties in existing conversion units. Hybrid fuels with a high bio-based content, fully compatible with conventional combustion systems, would be the output.

Of course, co-feeding intermediates, which are derived from lignocellulosic biomass, into conventional refineries strictly requires compatibility with the refining processes and, especially, the reliability of the intermediates' properties. This includes particularly the conversion of the solid matter into some liquids, because conventional refineries are used to liquid feedstock instead of solid ones. Furthermore, such conversion step incorporates the potential to increase the energy density from the loose vastly distributed biomass to the liquid intermediate, which would increase the distance over which the intermediate product might be transported economically. In the end at the refinery level, fuel qualities meeting the standards and fuel yields not diminished by intermediate-caused off-spec batches are the explicit goal.

This defines the idea behind the BioMates-concept, graphically represented in Figure 1: fast pyrolysis converts lignocellulosic, herbaceous feedstock to bio-oil, which is upgraded to a high-quality bio-based intermediate to be readily co-fed in a conventional refinery. The first step involves ablative fast pyrolysis (AFP), optionally enhanced by staged condensation and/or in-line-catalysis attached to the AFP-reactor to optimise the bio-oil with respect to the later refinery application. The resulting high energy density of the bio-oil enables a cost-efficient transport ("Rail & Road" in Figure 1), and this first processing step is preferably located in the vicinity of the biomass source in order to avoid long-distance transportation of low-density biomass. This decentralised bio-oil production will substantially contribute to strengthening rural areas. In the framework of circular economy, the use of the char (obtained as a by-product) as soil enhancer or fertilizer to be applied onto the field it originated from, will be investigated.

The second step, mild catalytic hydrotreating (mild-HDT), which follows the ablative fast pyrolysis of herbaceous biomass, is to be carried out preferably near the refinery that is intended to co-feed the produced intermediates. This allows for synergy effects, mainly by feeding excess hydrogen from the refinery – if available – into the mild catalytic hydrotreating plant, where it is used to turn the bio-oil into well-defined "Bio-based Intermediates" – the "BioMates". It ensures that critical properties such as acid value, oxygen content or sulphur content are guaranteed at any time, thus enabling "BioMates" to enter the refinery processes without any need of technical consideration on the operation or final product quality. The final aim is to provide intermediates with more or less invariant properties regardless of (herbaceous) biomass processed, regardless of region of origin and growing season. Applying solar-generated renewable make-up hydrogen and electrochemical compression of the recycled gas further bears the potential to reduce both carbon footprint and production costs of the bio-based intermediates.

Figure 1: Overall concept behind the BioMates project [1]

The proposed pathway for decarbonisation of transport fuels will be validated via so-called TRL 5-units [2] for pyrolysis and hydrotreatment, where Technological Readiness Level (TRL) 5 indicates technologies that are validated in an industrially relevant environment. This will allow the development of an integrated, sustainability-driven business case encompassing commercial and social aspects for the exploitation strategy. Prior R&D will be done in TRL 4-plants, denoting technologies validated in lab-scale.

The consortium that realises the collaborative project consists of

- Fraunhofer-Institute for Environmental, Safety, and Energy Technology UMSICHT from Oberhausen, Germany (coordinator),

- University of Chemical Technology Prague UCTP from Prague, Czech Republic,
- Ranido sro from Prague, Czech Republic,
- Centre for Research and Technology Hellas CERTH from Thessaloniki, Greece,
- HyET Hydrogen BV from Arnhem, The Netherlands,
- ifeu – Institute for Energy and Environmental Research GmbH from Heidelberg, Germany,
- Imperial College London from London, United Kingdom, and
- BP Europe SE from Bochum, Germany.

This manuscript is based on a project-related presentation given during the 7th International Conference on Engineering for Waste and Biomass Valorization–WasteEng2018 in Prague, Czech Republic. It aims at presenting the main results from the research stage of the project–improving quality and yield of pyrolysis liquids, finding optimal operating conditions for mild hydrotreatment, identifying suitable catalysts for mild hydrotreatment and designing a test system for electrochemical compression and purification already in a scale larger than typical laboratory equipment–before entering the scale-up activities to reach the anticipated technological readiness level (TRL) 5. The approach therefore is more practice-oriented and less scientific. The materials and method section gives an overview of the possible options for the process layout in the several steps from fast pyrolysis over mild hydrotreatment to electrochemical hydrogen compression and purification. The following section then provides the major results achieved from experimental research and in the conclusion section these results are summarized and evaluated to develop the overall process layout for the larger scale system.

2. Methods and Materials

2.1 Ablative Fast Pyrolysis

General dependencies in pyrolysis processes are summerized in a recent review by Kan et al. [3]. More specific, BioMates processing of herbaceous biomass starts with AFP, the general principle of which is depicted in Figure 2. Here, the raw material is pressed in inert atmosphere against a rotating, heated source at $\approx 550\text{ }^{\circ}\text{C}$, where it vaporises in less than 1 s. The primary products of pyrolysis–char and vapours–are separated and leave the reactor at different outlets. Cooling down to room temperature, the formed vapours separate into a liquid product and permanent gases. This liquid amounts to 40-70 wt.-% depending on operating conditions and feedstock material, and in the case of processing straw it results in only 10 % of the feedstock volume. It is necessary to remove the vapours from the hot zone quickly to prevent secondary gas phase reactions, which would lead to further cracking and thus resulting in more permanent gases and less condensibles. The reactor is fed with briquetted biomass – either straw or miscanthus – with a briquette diameter of 50 mm. The feed rate was about 5 kg/h. A more detailed description of the process of ablative fast pyrolysis is given elsewhere [4] and the laboratory plant (TRL4-unit) is discussed in [5]. Meanwhile, the cyclone for separating fly ash and fine char from the vapours leaving the pyrolysis reactor as described in [5] was replaced by a hot gas filter system, which substantially reduced the amount of residual solids in the final condensed liquids.

Figure 2: General principle of ablative fast pyrolysis [5]

AFP was chosen as primary conversion technology [5, 6] from many generally available developments for pyrolysis reactors [3, 7-9] due to three main reasons: it does not require any heat transfer material, it does not require a specific orientation of the reactor and it does not require grinding of the feedstock to very small particle sizes. As herbaceous biomass has a low volumetric energy density it is not possible to transport it over long distances to centralized conversion plants economically. Therefore, it seemed to be more economic to move the pyrolyzer around at least to the field margins where the feedstock originates from [10]. The principle of AFP for the conversion of woody biomass was developed by Lédé [11] and further developed for practical application by Pytec, a company from Hamburg [12, 13], and most recently picked up again by Luo [14, 15]. While Luo's group operates a small laboratory plant with only several grams of biomass for a batch operation of 3 min, Pytec operated a demonstration plant constructed in 20'-containers for the continuous conversion of wood chips of 250 kg h^{-1} , both groups aiming at transportable units to follow the availability of biomass feedstock and reducing the necessity of particle size reduction prior to pyrolysis.

The properties of the resulting bio-oil from AFP technology will be enhanced by means of fractionated condensation and/or “in-line catalysis”, also facilitating its subsequent upgrading. Here, in-line catalysis stands

for subjecting the primary vapours coming from the AFP-reactor to mesoporous or microporous materials, which are well-known means of deoxygenising pyrolysis vapours [16]. Alternatively, NREL develops a process to directly co-feed pyrolysis vapours from fast pyrolysis—either non-catalytic or catalytic—to a FCC reactor for the cracking of vacuum gasoil VGO in a refinery [17]. Although reported results with model compounds are quite satisfying, such approach would require the pyrolysis unit in large scale be located directly on the refinery site, which would be in principle be economic for woody biomass but quite unrealistic for low-density biomass like straw or energy crops. An overview on recent studies on in-situ and ex-situ catalytic fast pyrolysis can be found in [18]. With respect to the chosen type of pyrolysis reactor without any heat transfer material, in-situ catalytic pyrolysis is not possible in the framework of this study. Therefore, only ex-situ catalytic fast pyrolysis was considered further.

The ablative fast pyrolysis plant (TRL4-unit) originally was equipped with a single stage condensation followed by an electrostatic precipitator (ESP) for the removal of aerosols from the remaining permanent gases [5]. The condenser is operated at 4 °C and both condenser and ESP discharge the collected liquids into a joint catch tank. This setup catches all condensibles from the primary pyrolysis vapours in a single step and hence in a single containment. To gain more flexibility in the treatment of the primary vapours, an additional condenser and ESP, which both can be operated at elevated temperatures, and an externally heated fixed bed reactor for catalytic vapour treatment were acquired and can be installed at the pyrolysis plant to give a modular configuration shown in Figure 3.

Figure 3: Modular setup of laboratory ablative fast pyrolysis plant with in-line upgrade options [19]

The original setup with single stage condensation is depicted by pathway (A) in Figure 3. By inserting the reactor for catalytic vapour upgrade (see Figure 4) into the piping between the hot gas filter and the original condensation setup pathway (B) is configured. Alternatively, the additional setup of condenser and ESP (see Figure 5) can be inserted at the same place leading to pathway (C), a two-stage condensation setup with adjustable condensation temperature in the first stage between 50 to 85 °C. Finally, the catalytic reactor can be inserted between hot gas filter and two-stage condensation resulting in pathway (D).

Figure 4: Reactor for catalytic vapour upgrade [19]

Figure 5: AFP plant with two stage condensation (original single stage condenser and ESP in front) [19]

For preliminary experiments the reactor for catalytic vapour upgrade was installed in a side stream (in parallel with the original condensation setup). As the catalytic reactor originally was designed for use in the main stream only a small amount of catalyst was filled into the reactor. For these tests with lesser vapour streams (about 5 vol.-% of the produced total vapours), the unused “dead volume” of the reactor was filled with glass beads as shown in Figure 6. The temperature inside the reactor was measured at the end of the catalyst bed. The upgraded vapours were condensed in a single step by using a coil condenser and an electrostatic aerosol precipitator. For producing a reference sample, the total reactor volume was filled with glass beads for minimizing effects for different vapour residence times. The temperature at the outside of the reactor (electrical resistance heaters) was kept constant at 400 °C. For each catalyst tested, a set of condensate samples was taken. After about 90 min time on stream the collection flask below condenser and ESP was changed repeatedly resulting in samples up to 19.5 h time on stream. As the pilot plant can be operated only for 4 to 5 h per workday, the whole testing time had to be split into several experiments. One experiment consists out of 1-3 samples. The mass collected and some analytic parameters for each catalyst were calculated based on the associated samples.

Figure 6: Experimental setup for catalytic vapour upgrade operated in the side stream of pyrolysis plant [19]

Two different herbaceous feedstocks were used for all experiments in different plant layouts: a mixture of wheat/barley straw (50 wt.-% wheat and 50 wt.-% barley straw) supplied by Erhard Meyer, Hude-Vielstedt, under the trade name “Strohfix – Gerste” and Miscanthus x giganteus supplied by the company Sieverdingbeck, Velen-Ramsdorf, Germany, www.sieverdingbeck-agrar.de, under the trade name “Miscanthus Häcksel Premium”. Proximate and ultimate analysis of both feedstocks are given in Table 1.

Table 1: Proximate and ultimate analysis of biomass feedstock applied for bio-oil production [1]

The aim of catalytic vapour upgrade is to reduce the oxygen content of the liquid organic compounds, e.g. by decarboxylation and decarbonylation, to reduce their polarity and the amount of acids, aldehydes and ketones, as these components greatly affect the quality and storability of the condensates. six different materials were used as catalysts in this experimental study. Typically, zeolite and other solid acid materials are used for ex-situ catalytic pyrolysis [20], or mesoporous materials [16]. As example for porous materials, two different activated carbons (SC40 and SC44) were used. The main difference between both activated carbons (AC) is their surface area and pore size distribution. In future, it is intended to produce activated carbon catalysts by using the fine char of the pyrolysis process. As example for solid acid materials, γ -Al₂O₃ and HZSM-5 were used. The zeolite HZSM-5 was further modified by adding Ni in two different amounts on the basic structure. SC40 and SC44 were commercially available from Silcarbon Aktivkohle GmbH (Kirchhundem, Germany). The γ -Al₂O₃ catalyst was purchased from Thermo Fisher (Kandel) GmbH (Karlsruhe, Germany). The zeolite catalyst, HZSM-5, was purchased from ACS Material LLC (Pasadena, USA) and had a silica/alumina molar ratio of 38. Two modified zeolite catalysts, HZSM-5/5%Ni and HZSM-5/10%Ni, were produced by the project partner Ranido sro (Prague, Czech Republic) by adding 5 wt.-% and 10 wt.-% of nickel ions, respectively, by adding an aqueous solution of Ni(NO₃)₂ followed by drying and calcination, leaving NiO as predominant species on the HZSM-5 base material. To prepare the aqueous solution 247.8 mg Ni(NO₃)₂·6H₂O per gram HZSM-5 were used resulting in a Ni-loading of 5 %, as the solution was completely adsorbed on the catalyst surface. For the material with 10 % loading, the procedure was repeated. The use of nickel as additional compound on the zeolite surface was chosen, as there are hints that nickel reduces the tendency of coking [21]. The activated carbons and γ -Al₂O₃ were used as pellets and the zeolites as extrudates. The results from catalyst characterisation are summarised in Table 2. From earlier experience with the development of the Greasoline[®] process for decarboxylation of vegetable oils and fats over activated carbon, a temperature range from 350 °C to 450 °C was found to be optimal [22] and therefore a value of 400 °C was chosen for the whole set of experiments for both types of activated carbon. To keep the results comparable on first approach, all other catalysts were tested at this temperature also.

Table 2: Characteristic values of applied catalysts

2.2 Mild Hydrotreatment

Mild catalytic hydrotreating within the scope of the present project follows a one-step-approach that has several advantages when compared with the current state-of-the-art multiple hydroprocessing steps [23, 24]. A recently developed alternative to stabilization prior to deep hydrodeoxygenation is the use of solvents in a single step approach. Potential solvents are either ethanol or hydrotreated bio-oil [25]. The aim for such process still is to produce finished fuel blendstock which are low in oxygen.

The main advantage of the mild hydrotreatment suggested in this study is the significant reduction of the associated H₂ consumption, which is estimated to render at least 70 % decrease of the conversion cost over the conventional approach for up-grading pyrolysis bio-oils completely to finished fuels.

Tailor-made catalyst development is performed by Ranido sro in order to support and optimise mild hydrotreating. To test the catalysts developed by Ranido sro and to compare the results to the performance of commercially available standard hydrotreatment catalysts University of Chemistry and Technology Prague operates a continuous test rig for mild catalytic hydrotreatment, which is shown in Figure 7.

Figure 7: Continuously operated test rig for mild catalytic hydrotreatment

The largest piece of equipment placed in the upper left corner of the picture is the well-insulated and electrically heated fixed bed reactor with an inner diameter of 23 mm, a length of 320 mm and a catalyst loading of typically 55 g. The upper right corner shows the hydrogen supply line equipped with a mass flow controller. Hydrogen can be fed to the reactor with a pressure of up to 8 MPa and typically a feed flow rate of 90 l h⁻¹ at standard temperature and pressure was applied (equivalent to 8.1 g h⁻¹). The balance in the middle of the picture holds the bottle with the liquid feed and in the lower right corner the liquid feed pump can be seen. Typically, 55 g h⁻¹ of liquid feed solution is pumped to the reactor resulting in a weight hourly space velocity of 1 h⁻¹. Both hydrogen and liquid feed enter the reactor at the top and pass through a heating zone within the reactor without catalyst. Subsequently, the gas/liquid-mixture passes in concurrent flow through the catalyst bed. The product stream leaving the reactor is cooled, depressurized and liquid and gas are separated. The liquid product is collected in the glass bottle shown in the bottom part slightly left from the liquid feed pump.

The commercial standard hydrotreatment catalyst was made available by Ranido sro and was a classical NiMo catalyst (6.9 wt.-% Ni and 27.7 wt.-% Mo on Al_2O_3 support). Because it is a sulphidized type of catalyst, 0.5 wt.-% dimethyl disulphide (DMS) was added to the liquid to keep the catalyst active. Such catalysts are widely applied in petroleum refineries in hydrotreating units to remove heteroatoms like sulphur, nitrogen, phosphorous and to lesser extent oxygen [26]. A review of recent developments in hydrotreatment of fast pyrolysis bio-oils was compiled by Elliott [27]. The materials used the most are sulphidized NiMo-catalysts supported by Al_2O_3 followed by other transition metals and precious metals. Therefore, commercial NiMo-catalyst was chosen as starting point for catalyst development.

Ranido sro also supplied two catalysts in a non-sulphidized state with either Ni or Co as active species on Al_2O_3 -support. In contrary to the typical test conditions, the non-sulphidized Ni catalyst was tested applying a weight hourly space velocity of 0.25 h^{-1} and a hydrogen supply of 45 l h^{-1} at standard temperature and pressure.

As bio-oil feedstock for the hydrotreatment experiments always the tarry phase of single stage condensation (pathway A in Figure 3) from the pyrolysis of wheat/barley straw (540°C , 50 bar, 80 rpm) was used. The test rig was operated continuously after filling a certain catalyst and activating it. The first operation, until stable conditions were obtained, were performed with straight-run gasoil. After this procedure, mild hydrotreatment was started with the given parameters (weight hourly space velocity and hydrogen feed rate and pressure) with the lowest temperature. After stable operation for some time the temperature was raised to the next value without replacing the catalyst with fresh one.

Five typical liquids from refinery – two finished fuels, gasoline and diesel, and three internal streams, straight run gas oil, light cycle oil and a mixture made of straight run gas oil and light cycle oil – were mixed with samples from mildly hydrotreated bio-oil.

2.3 Electrochemical Hydrogen Compression and Purification

The overall approach to reduce the carbon footprint of final transportation fuels requires – beneath using low carbon feedstock – to reduce the carbon footprint of all conversion steps as much as possible. Therefore, the hydrogen necessary for mild hydrotreatment should be produced from renewable resources like solar irradiation. As part of the concept of BioMates, hydrogen will be produced by water electrolysis powered from a photovoltaic system. The supply pressure of the hydrogen resulting from the electrolyser is much lower than the required inlet pressure at the hydrotreater. Instead of using a conventional adiabatic multistage mechanical compressor, the hydrogen is compressed electrochemically [28]. The working principle of electrochemical hydrogen compression is depicted in Figure 8.

Figure 8: Working principle of electrochemical hydrogen compression

Hydrogen is fed to the catalyst layer on the anode side (upper line Figure 8). Here the hydrogen molecules are oxidized to protons. The protons are transported through the proton exchange membrane due to the small electrical potential applied and the electrons are moved from one side to the other in the electrical circuit outside the membrane. In the catalyst layer on the cathode side (lower line) the protons are recombined with the electrons to hydrogen molecules again.

The process already starts with only 5 mV (when the pressures are leveled on both sides). The electrical current is related directly to the amount of hydrogen molecules transported through the membrane. Each molecule of hydrogen transported through the membrane requires two electrons moved through the outer electrical circuit, so the pump rate can directly be determined by only measuring the electrical current.

It is a technology without moving parts, and hence silent, but also less wear and tear. It is an isothermal compression process instead of an adiabatic process in ‘standard’ mechanical compression and hence has the potential to be more energy efficient.

To be efficient, the process of hydrotreatment operates with a large overspill of hydrogen. The majority of the hydrogen fed to the hydrotreater therefore leaves unconverted. This hydrogen needs to be recovered and recycled back to the hydrotreater inlet. Usually, a pressure swing adsorption is applied for hydrogen recovery/purification from the tail gas and repressurised by a mechanical compressor. Because the proton exchange membrane used in the electrochemical compressor can only transport hydrogen (or more precisely: protons), this technology is also capable of purifying and recompressing the hydrogen from the tail gas leaving the hydrotreater, since all other components in a gas mixture will not be transported through the membrane [29].

3. Results and Discussion

3.1 Ablative Fast Pyrolysis

The processes in the pyrolysis unit can be separated into two individual steps: the ablative fast pyrolysis itself resulting in pyrolysis char and pyrolysis primary vapours and the subsequent downstream processing of the pyrolysis vapours, occasionally changing its composition over a heterogeneous catalytic contact (catalytic vapour upgrade) and finally reclaiming the condensibles in liquid form after condensation and somehow releasing or using the remaining permanent gases. According to L    [11] the main operating parameters influencing biomass conversion rate (equal to operating capacity of the total unit) are hot surface temperature, hot surface rotational speed and force, which the biomass is pressed against the hot surface with. Over the last years many experiments with varying operating conditions have been performed using firstly beech wood [6] and secondly cereal straw mixture made of wheat and barley straw that now can be evaluated to verify L   's results from solid wood. The general principles could be verified, which is discussed in the following based on the straw material only. The main parameter determining the biomass conversion rate at the TRL4 ablative fast pyrolysis plant is the hydraulic pressure forcing the biomass against the hot surface. The correlation of ablation rate (= speed of movement of hydraulic piston towards hot surface) with hydraulic pressure is shown in Figure 9. The ablation rate is defined as the velocity of the hydraulic piston towards the hot surface and was determined by measuring the remaining length of the hydraulic piston sticking out of the reactor at the beginning and at the end of a 10 s period measured by a stop watch.

Figure 9: Ablation rate vs. hydraulic pressure for wheat/barley straw at constant temperature (556   C) and rotational speed (133 rpm)

In contrary to L   's results the dependence of ablation rate on hydraulic pressure is not linear but could best be correlated using a second order polynomial approach. The reason for the different behaviour might be provoked by the different structure of the biomass, as compressed herbaceous biomass consisting of hollow stems was used in this study instead of solid wood, which was applied by L   .

The second parameter influencing the ablation rate is the temperature of the hot surface. This influence is depicted in Figure 10, which reveals a linear dependency with a quite small slope over the relatively narrow band of experimental observations. So, the hydraulic pressure is much more decisive concerning ablation rate than the temperature of the hot surface.

Figure 10: Ablation rate vs. hot surface temperature for wheat/barley straw at constant hydraulic pressure (50 bar) and rotational speed (133 rpm)

The rotational speed of the hot surface has no influence on the ablation rate above a certain value while below the dependency is linear [11]. The reported threshold according to L    is a relative speed of 1.5 m s⁻¹, which correlates to 114 rpm at the pyrolysis unit used in this study. The majority of experiments was performed with a rotational speed of 133 rpm, which is far above the minimum rotational speed calculated from L   's publications required for finished influence of this parameter on ablation rate. A thorough parameter variation to assess the dependency of ablation rate on rotational speed could not be performed due to restricted resources. Only experiments with one differing rotational speed of 80 rpm were conducted, resulting as expected in a lower ablation rate (equal to 0.304 mm s⁻¹ with a hot surface temperature of 540   C and a hydraulic pressure of 50 bar) as it is significantly below the calculated inflection point of the dependency at 114 rpm.

In contrary to ablation rate or biomass throughput the operating conditions concerning rotational speed and hydraulic pressure have a negligible influence on mass distribution of the three products char, condensibles and permanent gases. The parameter that dominates the respective yields is hot surface temperature. Figure 11 shows the dependency of respective yields in the temperature range from 487   C to 581   C. With increasing temperature, the amount of char reduces linearly, resulting in an increasing amount of primary vapours. The amount of condensibles (recovered at 4   C from the primary vapours) within the primary vapours rises in the beginning and after passing through a maximum it decreases with further increasing temperature, which confirms the general results literature [8, 30]. The closure of mass balance is incomplete as there are losses ranging from 5.8 % at 487   C to 9.0 % at 581   C. Despite these losses, the general trends in yield can be observed and for the type and size of equipment used a mass balance closure of more than 90 % is quite satisfying. From the results, it becomes clear that the optimal temperature of the hot surface for highest yields in condensibles, which is the target product within the project BioMates, is in the range of 540   C. Therefore, all

further experiments also for miscanthus were performed with a temperature setpoint of 550 °C, which resulted in a hot surface temperature of about (545±5) °C.

Figure 11: Yield of main products as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

The operating temperature of the hot surface is not only the most decisive parameter influencing the liquid yield but also the dominant parameter, besides biomass composition and ash content, regarding chemical composition of the collected liquids. Figure 12 shows the water mass fraction of the total liquid as a function of hot surface temperature and Table 3 summarizes the lumped composition of organics contained in the liquid for the three experimental temperatures applied.

Figure 12: Water mass fraction as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

Table 3: Lumped composition of total condensibles for wheat/barley straw (50 bar, 133 rpm)

Figure 12 clearly shows that the water mass fraction of the collected liquids rises with increasing temperature, indicating that the char received at lower temperatures still contains larger amounts of carbohydrates (sugar oligomers), which decompose with higher operating temperature releasing water and forming fixed carbon. For the organic part of the liquid no general dependence on hot surface temperature can be observed. The compound with high molecular weight, which can't be detected with GC, are cracked with higher temperatures, so their mass fraction reduces with increasing temperature. Organic acids, ketones, furans, phenols and syringols all exhibit a more or less pronounced increase in mass fraction with increasing temperature, while guaiacols show a maximum, sugars a minimum and pyrans decrease steadily with increasing temperature.

Due to the high water mass fraction of the recovered liquids from the primary vapours these liquids undergo instantaneous phase separation into an aqueous phase with approximately 38 % of dissolved organics and a tarry phase with a water mass fraction between 19 % at 487 °C and 25 % at 540 °C and 581 °C. The tarry phase is used for further upgrading towards the reliable intermediates (BioMates) and the aqueous phase would be disposed of in commercial production of BioMates. Figure 13 shows a slight maximum of tarry phase yield in the range of 540 °C for the pyrolysis of wheat/barley straw. This again reveals that in this range of hot surface temperature the optimum value is located, not only from the perspective of ablation rate (biomass throughput), but also maximum yield of desired product.

Figure 13: Phase separation into aqueous and tarry phase as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

A first step towards higher quality of recovered main liquid product is the condensation in two consecutive condenser-ESP units with decreasing operating temperature. As the second condenser is operated at the same temperature (4 °C), the total amount of liquids is unchanged compared to a single condensation unit, as long as the pyrolysis unit is operated at the same conditions. However, in staged condensation the distribution of compounds between phases is not based on solubility as between aqueous and tarry phase for single stage condensation but on dew point. This leads to different mass yields of liquids from first and second stage and to different compositions or properties depending on the operation temperature of the first unit. Figure 14 shows that the amount of liquid recovered in the first stage decreases as expected with increasing operating temperature while naturally the amount of liquid condensing in the second stage behaves exactly vice-versa. Below an operating temperature of 65.8 °C, the liquid in the first condenser still separates into an aqueous and a tarry phase, while for temperatures equal or above the liquid product from the first stage is single phase. Figure 15 depicts that the water mass fraction of the condensate recovered in the first stage decreases steadily with increasing operating temperature of the first condensing unit and the total acid number passes through a slightly pronounced maximum value at about 66 °C.

Figure 14: Liquid yields in first and second stage as function of first condenser operating temperature for wheat/barley straw (540 °C, 50 bar, 80 rpm)

Figure 15: Water mass fraction and total acid number of liquid product in first stage as function of first condenser operating temperature for wheat/barley straw (540 °C, 50 bar, 80 rpm)

The recovery of organic compounds in the target product in staged condensation is better than in the tarry phase for single stage condensation as can be deduced from Table 4. When two separate phases appear in the first condenser (at temperatures below 65.8 °C), only the tarry phase can be further used for hydrotreatment, and here the lowest recovery of organics in the target phase occur. But as soon as the liquid retained from the first stage is a single phase liquid, the highest organics recovery is observed with only low decrease in recovery rate with further increasing temperature. Even at an operating temperature of 71.2 °C the organics recovery in first stage liquid is higher than in the tarry phase of single stage condensation. Therefore, an operating temperature between 66 °C and 70 °C is taken as optimal value for the production of pyrolysis condensates to be used as feedstock for mild hydrotreatment. Similar results were obtained for miscanthus with a minimum operating temperature of first stage condenser of 63.5 °C for obtaining single phase liquids.

Table 4: Water and organics distribution over recovered liquid products from wheat/barley pyrolysis (540 °C, 50 bar, 80 rpm)

The improvement of quality and quantity of the primary liquid product achieved with staged condensation only relates to compound separation due to their respective due points. No change is made to the chemical composition of the condensibles. Such a change is intended by catalytic vapour upgrade. The orienting experiments performed for this study in a side stream of the experimental pyrolysis facility represent pathway (B) in Figure 3. Due to coke formation, the activity of the catalysts decline over time on stream, until in the end no effect of vapour contact with the catalysts can be seen any more; the condensates are same as for pathway (A). All samples collected show phase separation into an aqueous phase and a tarry phase regardless of catalyst. The results of elemental analysis (CHN from direct measurement using cube analyser from Elementar, O calculated by difference and S, Cl from condensate of bomb calorimeter), water content (Karl-Fischer titration), total acid number (TAN, by titration) and higher heating value (HHV, experimentally determined using a bomb calorimeter) for the samples resulting from the first experiment are given for the different catalysts in Table 5 and 6 based on the whole bio-oil and the tarry phase only, respectively. The amount of organics given in both tables is calculated by difference from the measured water content assuming only water and organic compounds being present in the condensates. For comparison, classical transportation fuels like gasoline or diesel have an average composition of 86 wt.-% carbon and 14 wt.-% hydrogen. The oxygen concentration is below 2 wt.-% for gasoline (before the addition of ethanol) and even below 1 wt.-% for diesel.

Table 5: Average values (based on the total bio-oils of 1st experiment) performed with different catalysts at 400 °C [19]

Table 6: Average values (based on tarry phase of 1st experiment) performed with different catalysts at 400 °C [19]

1st experiment refers to the total of samples taken on the first day of plant operation after filling fresh catalyst. Each sample results from 90 min of operation and for analyses the samples of the first day were joined. Compared to the reference sample, which was taken from the same setup with the reactor completely filled with glass beads, all catalysts increased the total water content of the condensates (in other words reduced the content of organics), which means that all catalysts either remove part of the oxygen from the organic compounds as water and/or convert parts of the organic vapour compounds into non-condensable permanent gases. As a consequence, the carbon content and the higher heating value of all samples is lower and the oxygen content is higher than for the reference sample. Based on the tarry phase (see Table 6) some catalysts improve the quality. For SC40 and the zeolite catalyst with highest loading of Ni (HZSM-5/10%Ni), the organic content is at least the same (zeolite) or even higher (SC40), which indicates a lower polarity of the organic compounds, and for both catalysts the carbon and hydrogen contents as well as higher heating value (HHV) are higher and the oxygen content is lower as well as total acid number (TAN). Both these catalysts influence the relevant parameters to the right direction.

These results only refer to the initial activity of the catalysts as they were taken from the first experiment. With continuing time on stream, the properties of samples more and more approach the results gained from aqueous and tarry phase of single stage condensation. The deactivation of catalysts can mostly be correlated with carbon

deposition. The characteristic values of surface area and pore volume after the experiments are given in Table 7 and differ dramatically compared to the values for fresh catalysts (compare Table 2).

Table 7: Characteristic values of applied catalysts (after use)

The interpretation of the results from the side stream experiments is very difficult as already the amounts of sample mass for the very first sample differ largely from catalyst to catalyst (see Table 8), although the external settings were the same for all experiments. But due to different catalyst shapes the pressure drop within the catalyst bed is different. Also, over time bed porosity and hence pressure drop might change with different intensity for the catalysts. Therefore, the amount of primary pyrolysis vapour treated with catalyst contact might be very different for the miscellaneous catalysts.

Table 8: Total amounts of condensibles collected as 1st sample [19]

Experiments with the reactor for catalytic vapour upgrade in the main stream (pathway D in Figure 3) are currently underway to get a closed mass balance for yields in this setup. The results from side stream strongly indicate that a fixed bed reactor seems to be not the best choice, as quality of recovered liquid product changes fast with time on stream. A moving bed of catalyst, always having fresh catalyst on end of the bed and spent catalysts on the other might give constant properties of recovered liquids over time. If these properties are superior to the condensates from the first condensing unit in a setup following pathway C in Figure 3 needs to be evaluated in the future.

3.2 Mild Hydrotreatment

Here, only the most important results with respect to the overall project concept are reported. An in-depth analysis and discussion of the various experimental test series was published recently [31].

The most important parameter of product coming from mild hydrotreatment is the residual water mass fraction of the organic phase. Within the tested temperature range from 280 °C to 320 °C the sulphidized commercial catalyst performed best for all temperatures while the non-sulphidized Ni-catalyst resulted in equal water mass fraction at least for the highest temperature as can be seen in Figure 16.

Figure 16: Water mass fraction as function of reaction temperature for mild hydrotreatment

Figure 17 depicts the density and the kinematic viscosity of the organic phase after mild hydrotreatment. For both these properties the non-sulphidized Ni-catalyst performed best, because it gave lowest values, while the also non-sulphidized Co-catalyst gave highest values. The commercial sulphidized NiMo-catalyst produced products in between the two non-sulphidized catalysts.

Figure 17: Density and kinematic viscosity as function of reaction temperature for mild hydrotreatment

The degree of deoxygenation is increasing with temperature and always the highest for the commercial NiMo-catalyst, which is clearly to be seen from Figure 18. This value is based on the oxygen content in raw bio-oil and organic product phase, which was determined by elemental analysis. Again, the Ni-catalyst performs better compared to the Co-catalyst. Typically, the catalysts deactivate with increasing time on stream due to coke deposition and several poisoning mechanisms. Increasing temperature after a certain time on stream should overcompensate this deactivation. The commercial NiMo-catalyst behaves like expected, as the carboxylic acid number drastically drops with increasing temperature. Contrariwise, the carboxylic acid number in the products resulting from the non-sulphidized Ni- and Co-catalyst rise with increasing temperature, indicating a faster deactivation compared to the NiMo-catalyst. Potentially, the low sulphur concentration in the raw bio-oil is still more than tolerable for the non-sulphidized catalysts.

Figure 18: Carboxylic acid number and Degree of deoxygenation as function of reaction temperature for mild hydrotreatment

The commercial sulphidized NiMo-catalyst was used for an extended set of experiments with variation of hydrogen supply pressure from 2 MPa to 8 MPa and over a broader temperature range from 280 °C up to 360 °C. The resulting properties are summarized in Figure 19. With highest hydrogen pressure of 8 MPa and highest temperature of 360 °C very good results were achieved: the water mass fraction could be reduced to 0.36 wt.-%, the kinematic viscosity reached a value of 3.3 mm² s⁻¹, the density at 15 °C was as low as 0.89 kg dm⁻³ and the lower heating value came close to 40 kJ kg⁻¹.

Figure 19: Results of extended testing with commercial NiMo-catalyst (sulphidized)

Mild hydrotreatment converts the original bio-oil in the direction of transportation fuel but only to a certain amount. The bio-oil used in the parametric study (pyrolysis of straw mixture at 550 °C, 50 bar, 133 rpm, single-stage condensation with cooling liquid at 4 °C; tarry phase) had an atomic hydrogen to carbon ratio of about 1.2 and an atomic oxygen to carbon ratio of about 0.225. The best BioMates achieved with 8 MPa hydrogen pressure, a weight hourly space velocity for the bio-oil of 1 h⁻¹ and commercial NiMo-catalyst in sulphidized form reached a H/C-ratio of 1.65 and an O/C-ratio of 0.025. [31] Diesel for comparison could be represented by an average formula of CH₂ which gives a H/C-ratio of nearly 2 and virtually zero for the O/C-ratio.

The sample with best properties resulting from hydrotreatment with commercial NiMo-catalyst under a hydrogen pressure of 8 MPa at 360 °C reactor temperature was used for miscibility tests with five liquids from a refinery. As can be seen from Figure 20, raw bio-oil (tarry phase from single stage condensation of primary vapours from wheat/barley straw pyrolysis) was immiscible with all five liquids. On the other hand, hydrotreated product – the targeted “BioMate” – was fully miscible with gasoline and straight run gas oil and to a lower degree with diesel, light cycle oil and the mixture made of straight run gas oil and light cycle oil.

Figure 20: Miscibility tests with typical liquids from refineries with raw bio-oil (B, left) and organic product from mild hydrotreatment (P, right)

Presently, the concept of co-processing pyrolysis condensates in standard petroleum refineries is investigated by several groups. The usual choice of entry point is the feeding system of a fluid catalytic cracking reactor (FCC), where vacuum gasoil is reduced in molecular weight to increase the refineries output of transportation fuels. This approach is evaluated in depth in laboratory [32, 33] as well as already in pilot plant operation [34, 35]. The major drawback of this approach is the fact that the majority of carbon from the biogenous feedstock ends up in the coke produced in the FCC. The usual distribution of carbon entering the FCC between gases, desired liquid products like gasoline or light cycle oil and coke is not reproduced with the bio-oils, which has been proven by ¹⁴C-analyses in laboratory as well as in pilot testing [34, 36]. For instance, when 10 % pyrolysis condensates were fed to the pilot FCC unit at Petrobras, only 2 % of the carbon contained in the liquid products were biogenic [34]. The miscibility of mildly hydrotreated pyrolysis condensates with light cycle oil would allow to feed the biogenic feedstock downstream the FCC and by that avoiding the huge losses of organic carbon to the undesired coke fraction.

3.3 Electrochemical Hydrogen Compression and Purification

Previous models of electrochemical hydrogen pressurisation systems were optimized for compression only. A delivery pressure of 100 MPa on the cathode is possible and done at HyET Hydrogen [28] over one single membrane and recently also with only 0.5 MPa feed pressure on the anode side.

The new platform is designed for both compression and purification, where in contrary to compression of pure hydrogen only the anode side of the system needs a continuous outlet for the gas components besides hydrogen. A hydrogen purity of 99.5 % or even higher is already proven [29]. To increase the total flow of hydrogen, single cells are stacked with interconnectors between adjacent cells to give a multiple cell system. This system is shown in Figure 21 with the stack as the main unit on top of the cabinet and equipped with necessary measurement and control system.

Figure 21: Multiple cell test system for hydrogen compression and purification

The new platform was tested intensively in laboratory with single cell and multiple cell arrangements. The key performance indicators set out in the BioMates proposal consider the maximum hydrogen delivery pressure, the specific energy demand for compression on one side and for purification on the other side and for purification

mode the recovery rate, which is defined as hydrogen flow rate at cathode outlet divided by hydrogen feed flow rate to the anode side. The target values and the actually achieved ones are given in Table 9.

Table 9: Key performance indicators for electrochemical hydrogen compression and purification

The target for final pressure is by far more than fulfilled, the target for specific energy demand for compression is met and that for purification is overachieved. For a single cell arrangement the target for recovery rate is also met, but for the multiple cell arrangement further improvement is necessary. For the experimental validation of the process within the BioMates project, less than 0.5 kg H₂ per day is required. The recent stack is able to provide up to 10 kg H₂ per day.

This mobile testing system will be used at partner CERTH in Thessaloniki on one side to compress hydrogen from a water electrolysis system powered by a photovoltaic system to the required feed pressure of the hydrotreater and on the other hand to recover the hydrogen overspill from hydrotreater off-gas and recycle it to the feed stream of the hydrotreater. This is to verify the key performance indicators determined in the laboratory under relevant industrial environment.

4. Conclusions

Biomass ablative fast pyrolysis was studied intensively in a TRL4 laboratory plant with two different herbaceous feedstocks: a mixture of wheat and barley straw as a model compound for agricultural residues and *Miscanthus x giganteus* as model compound for dedicated energy crops, but only values for straw were presented for the sake of simplicity. In general, the results for *Miscanthus* were similar. The conversion process towards the target product organic liquid can be subdivided into two distinct steps: the pyrolysis itself, resulting in residual char and primary pyrolysis vapours, and vapour downstream processing to recover the liquid product. From all experimental data available it can be concluded that the main parameter influencing yield and composition of the target liquid is the temperature of the hot surface in the pyrolysis reactor. Best results are achieved with a temperature around 540 °C, where a weakly pronounced maximum in liquid organic yield could be observed. The second operating parameter mainly influencing ablation rate and by that biomass throughput is the hydraulic pressure with which the biomass briquettes were pressured against the hot surface. Different from literature, where a linear correlation between pressure and ablation rate was reported for solid wood [11], a second order polynomial correlation could be deduced from the experimental results, meaning that with increasing hydraulic pressure the ablation rate steadily increases but with decreasing gradient (significance). The optimum value was determined to be 50 bar. The third parameter discussed in literature [11], rotational speed of the hot surface used for ablation, turned out to be of minor importance. The maximum rotational speed of 133 rpm was not necessary and could be reduced to around 80 rpm without significant loss in biomass throughput based on mass flow rate although the ablation rate only was about half the value compared to the higher rotational speed.

For the downstream processing of pyrolysis primary vapours four different approaches were defined beforehand and three of them were investigated. The easiest way to recover all condensibles at once is to completely cool down the vapours with cooling medium at 4 °C and subsequently remove aerosols from the remaining permanent gases by means of an electrostatic precipitator. Due to the higher amount of ash-forming minerals and lower amount of lignin in herbaceous biomass compared to wood, the recovered liquid from such a unit always splits into two phases – an aqueous phase with approximately 30 wt.-% of dissolved organic compounds and a tarry phase with still about 21 wt.-% water content. The aqueous phase needs to be disposed of due to its high organic content, which is lost with regard to the final application as refinery co-feed. The tarry phase is highly viscous and behaves like a sludge instead of a smooth liquid. The final yield of organic matter in the tarry phase of this first recovery approach is 18 wt.-% based on as received basis of the biomass with an average water mass fraction of 8 wt.-%.

The second approach for downstream processing was a setup applying two units in a row with a condenser and an electrostatic precipitator each. The second unit was operated again with cooling medium of 4 °C and the first unit was operated with a feed temperature of the cooling medium between 40 °C and 100 °C. With low residual vapour temperature leaving the first unit, also the liquids collected in the first unit showed phase separation. With a vapour temperature of 65.8 °C or above for straw and 63.5 °C or above for *Miscanthus*, single phase product liquids could be recovered from the first stage condensing unit. With this approach, the highest yield of organic compounds in the target liquid could be achieved. Based on as received biomass feedstock this yield was found to be 21 wt.-%.

Six different catalysts were tested in a fixed bed reactor for catalytic vapour upgrade followed by a single stage condensation unit in a side stream of the pyrolysis plant. Only for two catalysts – commercial activated carbon

SC40 and HZSM-5/10%Ni – a slight improvement in liquid properties, expressed by higher organics concentration in the liquid, higher carbon and hydrogen content, lower oxygen content, lower total acid number and increased higher heating value. All other catalysts even deteriorated the liquid quality. The amounts of collected sample volume gave hints that the final yield of liquids for further processing in hydrotreatment might be much less compared to two-stage condensation. With increasing time on stream the activity of the tested catalysts ceased more and more and the quality of the collected liquid samples approached that known from single stage condensation unit. From these results it can be concluded that even with the best catalysts tested the reduction in organic yield is not compensated by properly improved liquid quality. Therefore, the catalytic vapour upgrade is not a feasible option for the time being. In addition, the fixed bed reactor setup seems to be inappropriate because of the observed fast deactivation of the catalysts. A moving bed for continuous feeding of fresh catalyst and removal of spent catalyst suggests itself for future investigation.

Tarry phase liquid from single stage condensation based on straw pyrolysis was used in a fixed bed concurrent TRL3 test rig for mild hydrotreatment. Newly developed catalysts based on metallic Ni and Co as active components on an Al₂O₃-support – avoiding the necessity for sulphur addition – were tested in comparison with a commercial NiMo-catalyst in sulphidized form. Although the new catalysts showed high initial activity and for some parameters even better results than the commercial one, they deactivated much faster than the commercial one. Therefore, it can be concluded that the low amount of sulphur present in the tarry phase liquid from ablative fast pyrolysis still has detrimental effect on non-sulphidized catalysts. As long as no measures are found to stabilize the performance of non-sulphidized catalysts, standard commercial NiMo-catalysts, which require the addition of dimethyl disulphide to the liquid feedstock, are the best choice for hydrotreatment. The main parameters in hydrotreatment influencing yield and quality are hydrogen supply pressure and operating temperature. Using the commercial NiMo-catalyst these two parameters were varied over a large range: hydrogen supply pressure from 2 MPa to 8 MPa and operating temperature from 280 °C to 360 °C. All properties describing the quality of the liquid product improved with increasing hydrogen pressure and increasing operating temperature – thus increased severity of hydrotreatment conditions.

Five liquids from petroleum refinery were used for preliminary miscibility tests with tarry phase from ablative fast pyrolysis directly and hydrotreated liquid product from most severe conditions. While raw bio-oil (tarry phase) showed no miscibility at all, the hydrotreated product was miscible with gasoline and straight run gas oil. Additionally, it was partly miscible with the remaining three liquids diesel, light cycle oil and a mixture made of straight run gas oil and light cycle oil. These preliminary tests lead to the conclusion that BioMates are most likely to be co-processed in a petroleum refinery with a larger share. The effect of introducing oxygenates in these streams may affect the efficiency of hydrotreating units downstream of the entry point, as these units usually remove other heteroatoms like sulphur, nitrogen or phosphorous from the fossil-based feed stream, which are virtually free of oxygen. Therefore further investigations are necessary to evaluate how many oxygen can be introduced to the streams by adding BioMates without compromising the hydrotreater efficiency too much.

Further economic and ecological improvement of the hydrotreatment process may be possible by implementation of electrochemical compression and purification. In the case of purification of hydrogen from hydrotreatment off-gases, the single electrochemical device replaces a pressure swing adsorption unit with several pressure vessels in parallel (at least four) and many valves. The electrochemical compression works under isothermal conditions instead of adiabatic conditions for mechanical compression. This opens the possibility for an energy efficient compression, which could be proven in laboratory environment: high pressure ratio, high delivery rate and moderate energy demand both for compression and purification.

The BioMates project idea was proven in laboratory environment in TRL4 (pyrolysis) and TRL3 (hydrotreatment) equipment. The challenge for the remaining project period and the progress of the process as a whole is to validate the process chain in equipment with TRL5.

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Tables with headings:

Table I: Proximate and ultimate analysis of biomass feedstock applied for bio-oil production [1]

	Wheat/Barley straw	Miscanthus
Proximate analysis		
Water (wt.-%)	6.8	11.9
Ash (wt.-%, mf)	3.1	2.5
Volatiles (wt.-%, daf)	75.4	75.4
Fixed carbon (wt.-%, daf)	24.6	24.6
HHV (MJ/kg, daf)	19.3	19.4
Ultimate analysis		
C (wt.-%, daf)	49.1	50.6
H (wt.-%, daf)	5.8	4.1
N (wt.-%, daf)	0.4	-
O (wt.-%, daf) [†]	44.7	45.3
S (ppm, daf)	767	347
Cl (ppm, daf)	2,526	719
K (ppm, daf)	13,725	2,423
Ca (ppm, daf)	1,713	1,669
Mg (ppm, daf)	349	237
Na (ppm, daf)	193	16
P (ppm, daf)	-	650

mf – moisture-free basis;

daf – dry and ash-free basis

[†] calculated by difference

Table 2: Characteristic values of applied catalysts (fresh)

Catalyst	Diameter [mm]	BET surface area [m ² g ⁻¹]	Total pore volume ^a [cm ³ g ⁻¹]	Average pore diameter ^b [nm]
SC40	4.0	1993.71	1.11	2.30
SC44	4.4	1430.97	0.74	2.06
γ-Al ₂ O ₃	3.2	259.76	0.84	13.00
HZSM-5	2.0	347.09	0.34	3.92
HZSM-5/5%Ni	2.0	321.36	0.31	3.85
HZSM-5/10%Ni	2.0	293.26	0.27	3.71

^a Determined by single point N₂-adsorption at P/P₀ = 0.99.^b Determined by N₂-adsorption.

Table 3: Lumped composition of total condensibles for wheat/barley straw (50 bar, 133 rpm)

Chemical substances (wt.-% based on wet basis)	Hot surface temperature (°C)		
	487	540	581
Nonaromatic acids	6.03	6.92	10.66
Nonaromatic aldehydes	0.4	0.45	0.35
Nonaromatic ketones	5.51	6.44	10.85
Furans	1.8	1.82	2.08
Pyrans	0.09	0.08	0.02
Phenols	0.68	0.84	1.19
Guaiacols	1.99	2.54	1.03
Syringols	1.47	1.85	2.14
Sugars	1.71	1.54	2.01
GC non-detectable	29.1	28.78	16.44

Table 4: Water and organics distribution over recovered liquid products from wheat/barley pyrolysis (540 °C, 50 bar, 80 rpm)

	Water mass fraction [%]	Organics mass fraction [%]
Lumped liquid composition	49	51
Single stage condensation		
Aqueous phase	40	36
Tarry phase	9	15
Two stage condensation, FSCT = 62.8 °C		
Aqueous phase, first stage	18	10
Tarry phase, first stage	6	34
Second stage	25	7
Two stage condensation, FSCT = 65.8 °C		
First stage	15	42
Second stage	34	9
Two stage condensation, FSCT = 68.8 °C		
First stage	11	41
Second stage	38	10
Two stage condensation, FSCT = 71.1 °C		
First stage	4	39
Second stage	45	12

FSCT = First Stage Condensation Temperature

Table 5: Average values (based on the total bio-oils of 1st experiment) performed with different catalysts at 400 °C [19]

	RS	SC40	SC44	γ -Al ₂ O ₃	HZSM-5	HZSM-5/5%Ni	HZSM-5/10%Ni
Time on stream (h)	1.5	3	1.5	4.5	3	3	4.5
Organics (wt.-%)	49.5	27.1	44.4	46.1	48.9	47.3	47.8
C (wt.-%)	30.5	15.1	25.8	26.8	28.4	28.5	30.0
H (wt.-%)	8.1	10.3	9.7	8.8	8.8	8.9	9.9
N (wt.-%)	0.5	0.3	0.4	0.5	0.4	0.4	0.5
O (wt.-%) ¹	60.9	74.3	64.1	63.9	62.4	62.2	59.6
S (wt.-%)	0.03	0.01	0.02	0.02	0.03	0.02	0.03
Cl (wt.-%)	0.02	0.02	0.01	0.02	0.03	0.03	0.03
TAN (mg KOH g ⁻¹)	71.4	74.7	85.1	81.4	86.5	70.0	64.5
HHV (MJ/kg ⁻¹)	12.8	6.0	10.9	10.4	11.3	12.3	12.7

RS: reference sample;

¹ O (wt.-%) = 100 (wt.-%) – C (wt.-%) – H (wt.-%) – N (wt.-%)Table 6: Average values (based on tarry phase of 1st experiment) performed with different catalysts at 400 °C [19]

	RS	SC40	SC44	γ -Al ₂ O ₃	HZSM-5	HZSM-5/5%Ni	HZSM-5/10%Ni
Time on stream (h)	1.5	3	1.5	4.5	3	3	4.5
Organics (wt.-%)	83.7	93.1	76.7	84.1	82.1	82.1	83.7
C (wt.-%)	57.6	67.8	49.8	56.4	55.3	55.3	58.2
H (wt.-%)	7.6	8.7	8.7	8.1	8.4	8.0	8.0
N (wt.-%)	0.7	0.7	0.7	0.7	0.7	0.6	0.8
O (wt.-%) ¹	34.1	22.8	40.8	34.8	35.6	36.1	33.0
S (wt.-%)	0.05	0.02	0.04	0.04	0.05	0.04	0.05
Cl (wt.-%)	0.02	0.01	0.01	0.02	0.02	0.02	0.02
TAN (mg KOH g ⁻¹)	66.7	49.6	81.1	92.0	98.8	62.6	57.2
HHV (MJ kg ⁻¹)	24.2	29.6	20.5	23.2	23.0	24.3	24.5

RS: reference sample;

¹ O (wt.-%) = 100 (wt.-%) – C (wt.-%) – H (wt.-%) – N (wt.-%)

Table 7: Characteristic values of applied catalysts (after use)

Catalyst	Diameter [mm]	Time-on- stream [h]	BET surface area [m ² g ⁻¹]	Total pore volume ^a [cm ³ g ⁻¹]	Average pore diameter ^b [nm]
SC40	4.0	21	nd	nd	nd
SC44	4.4	10.5	8.09	0.01	2.82
γ -Al ₂ O ₃	3.2	9	84.51	0.21	9.98
HZSM-5	2.0	10.5	46.31	0.08	6.48
HZSM-5/5%Ni	2.0	12	nd	nd	nd
HZSM-5/10%Ni	2.0	10.5	nd	nd	nd

^a Determined by single point N₂-adsorption at P/P₀ = 0.99.^b Determined by N₂-adsorption.

nd: Not determined

Table 8: Total amounts of condensibles collected as 1st sample

	RS	SC40	SC44	γ -Al ₂ O ₃	HZSM-5	HZSM-5/5%Ni	HZSM-5/10%Ni
Total liquids (g)	340	63	414	68	559	448	288
Aqueous phase (g)	263	59	268	60	375	326	210
Aqueous phase (%)	77.4	93.7	64.7	88.2	67.1	72.8	72.9
Tarry phase (g)	77	4	146	8	184	122	78
Tarry phase (%)	22.6	6.3	35.3	11.8	32.9	27.2	27.1

Table 9: Key performance indicators for electrochemical hydrogen compression and purification

Key Performance Indicator	Target	Achieved	
		Single cell	Multiple cells
Pressure [MPa]	15	70	>40
Energy demand compression [kWh kg ⁻¹ H ₂]	4.0	4.0	4.0
Energy demand purification [kWh kg ⁻¹ H ₂]	6.0	5.3	5.3
Recovery rate [%]	80	80	50-70

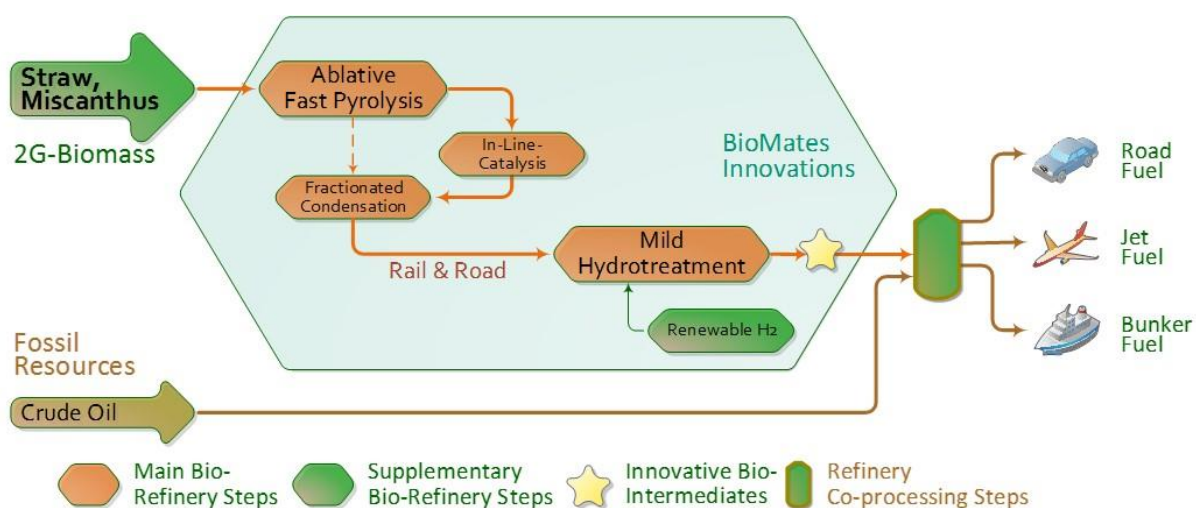


Figure 1: Overall concept behind the BioMates project [1]

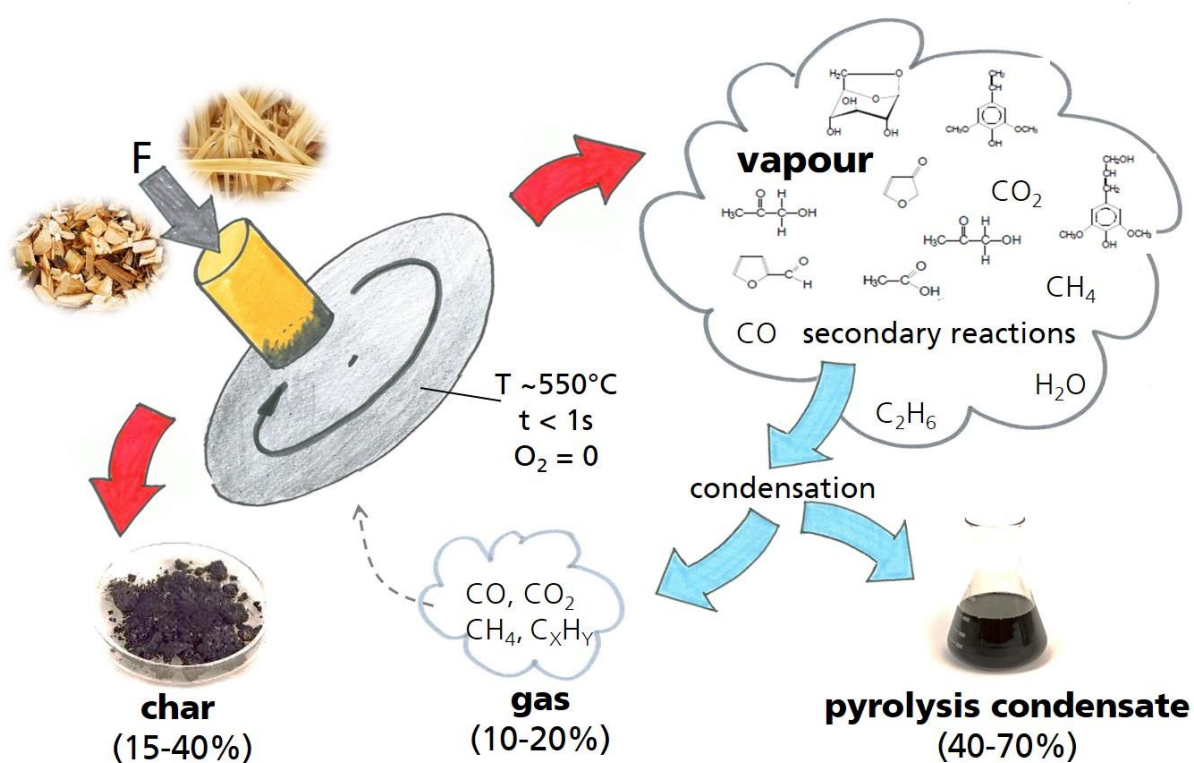


Figure 2: General principle of ablative fast pyrolysis [5]

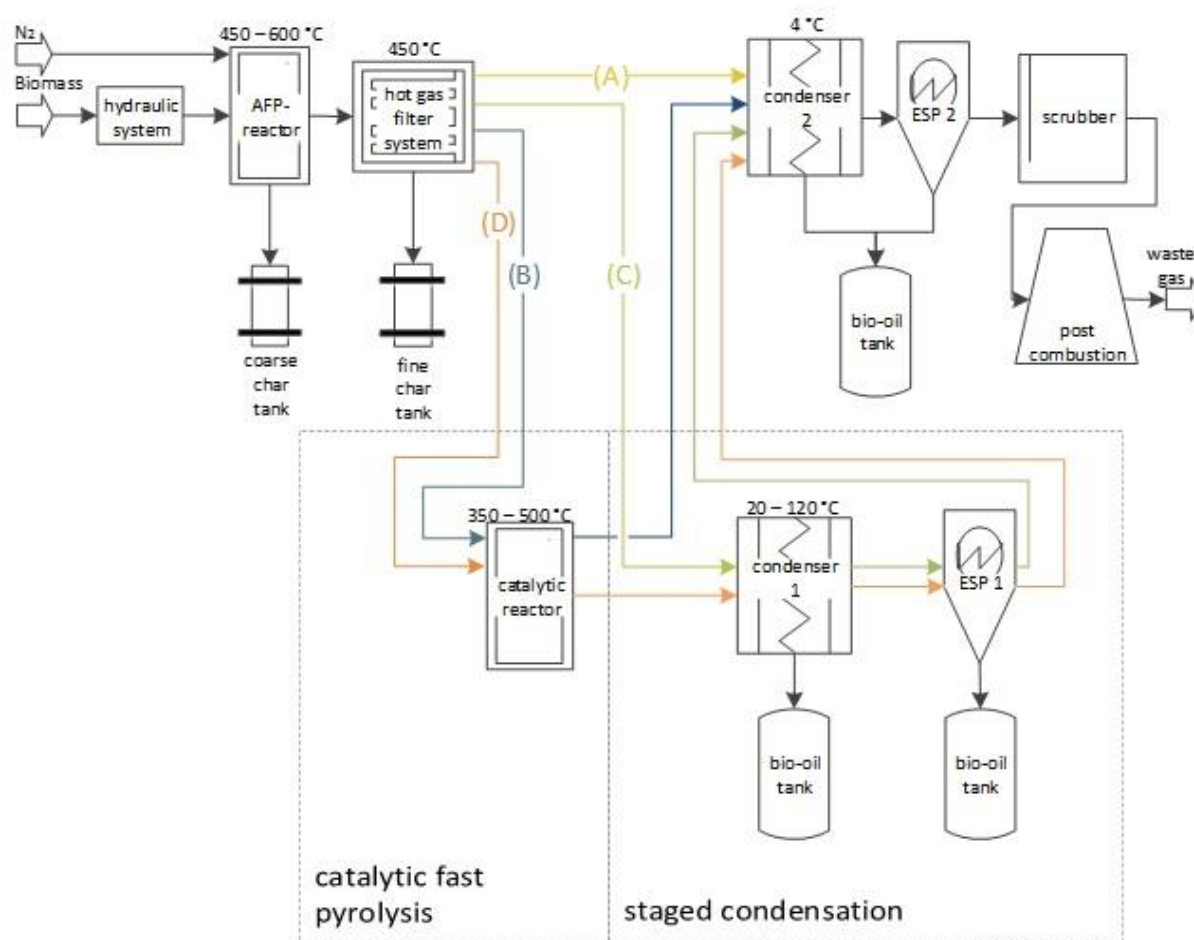


Figure 3: Modular setup of laboratory ablative fast pyrolysis plant with in-line upgrade options [19]



Figure 4: Reactor for catalytic vapour upgrade [19]



Figure 5: AFP plant with two stage condensation (original single stage condenser and ESP in front) [19]

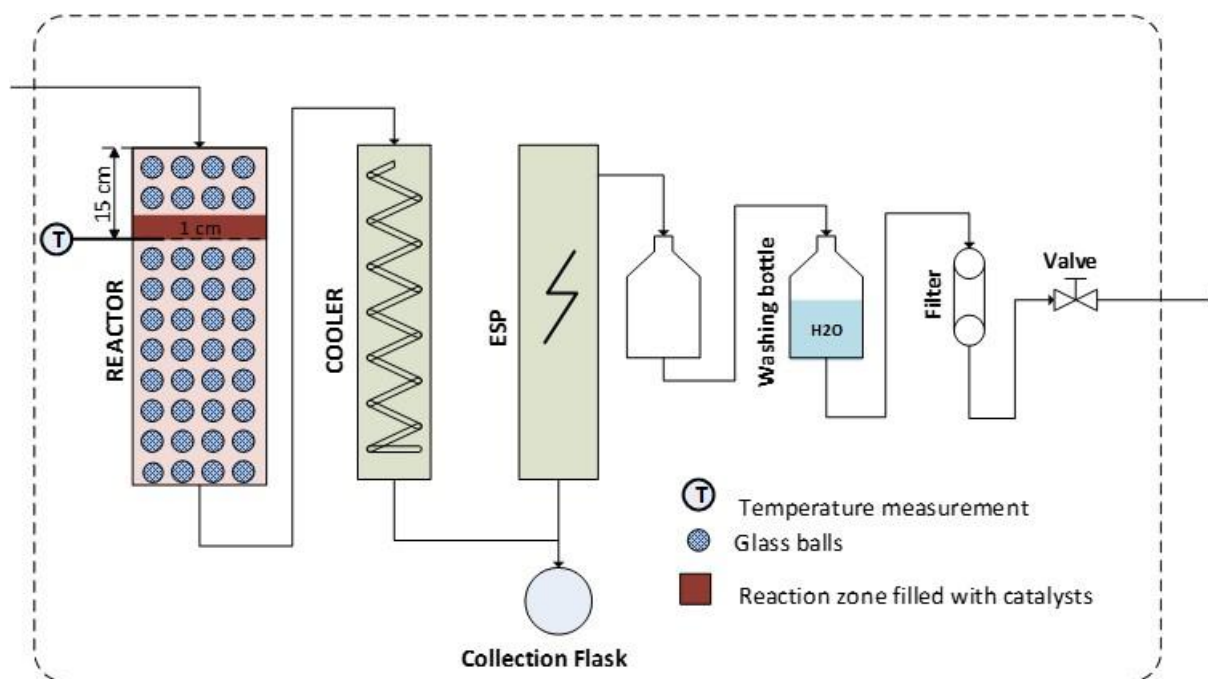


Figure 6: Experimental setup for catalytic vapour upgrade operated in the side stream of pyrolysis plant [19]



Figure 7: Continuously operated test rig for mild catalytic hydrotreatment

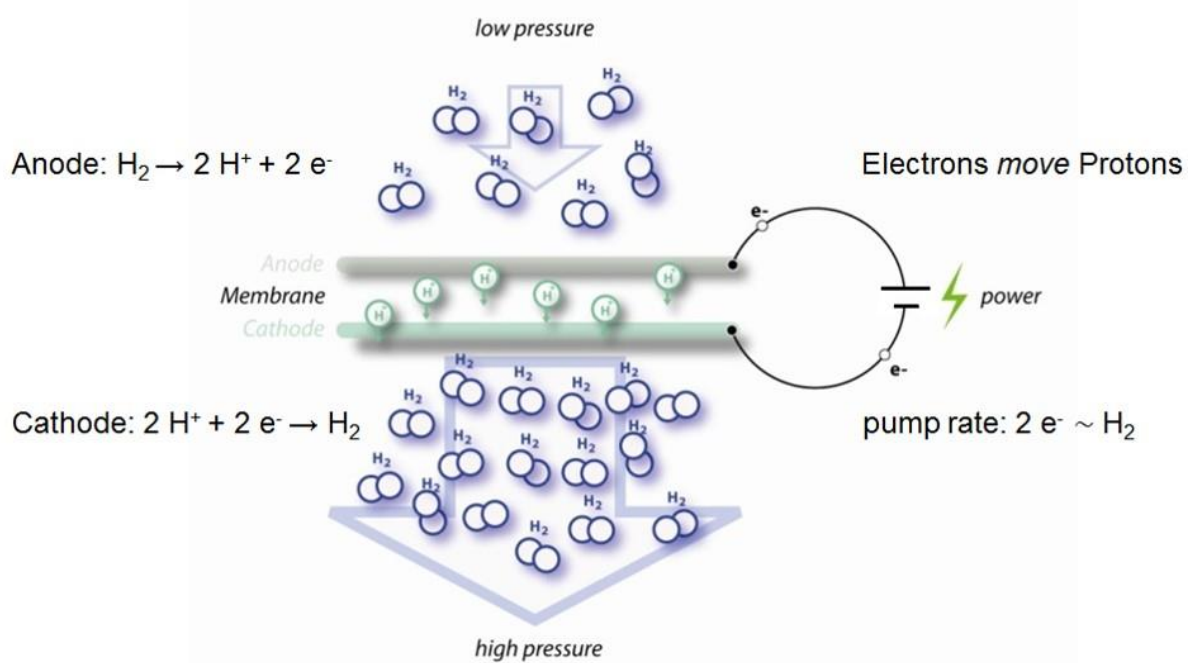


Figure 8: Working principle of electrochemical hydrogen compression

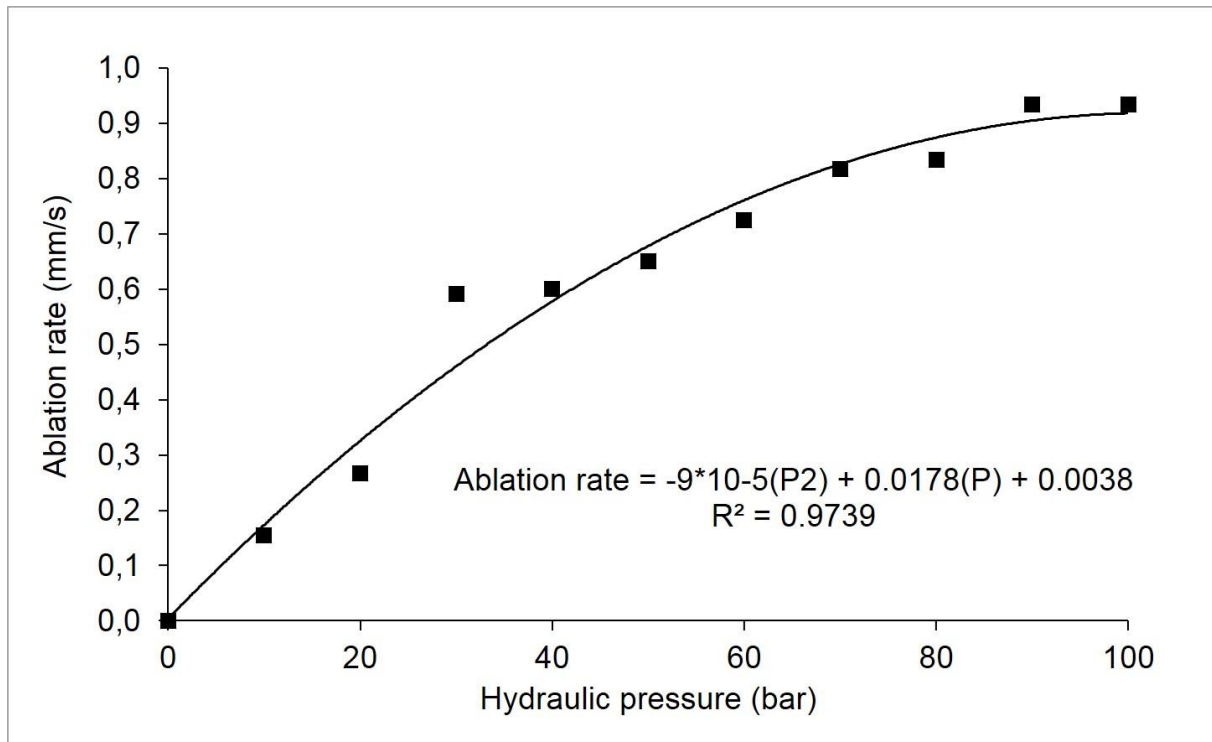


Figure 9: Ablation rate vs. hydraulic pressure for wheat/barley straw at constant temperature (556 °C) and rotational speed (133 rpm)

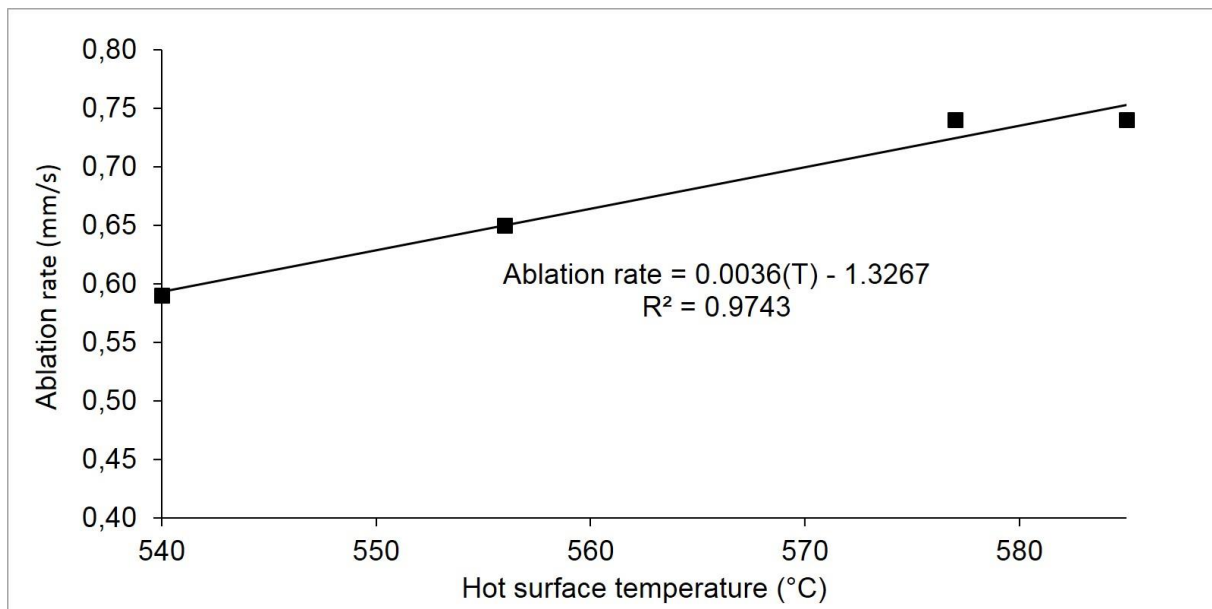


Figure 10: Ablation rate vs. hot surface temperature for wheat/barley straw at constant hydraulic pressure (50 bar) and rotational speed (133 rpm)

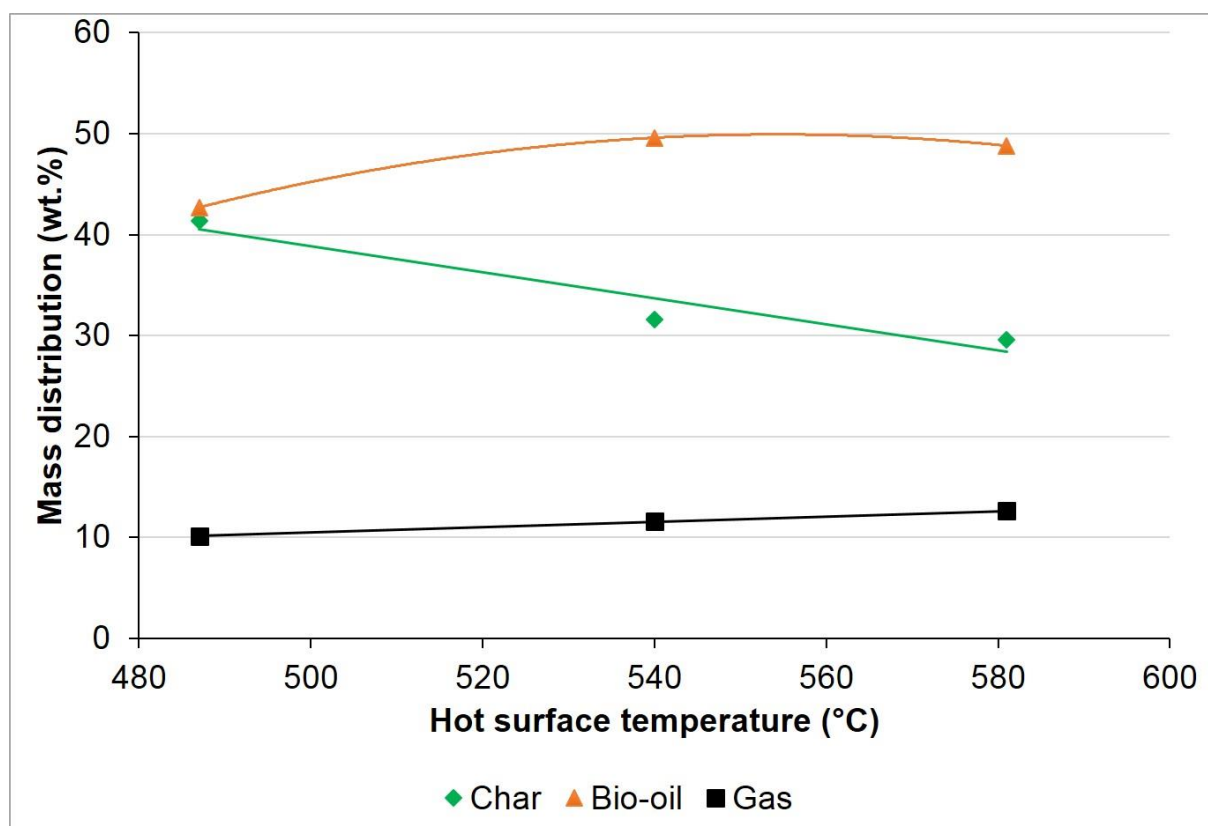


Figure 11: Yield of main products as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

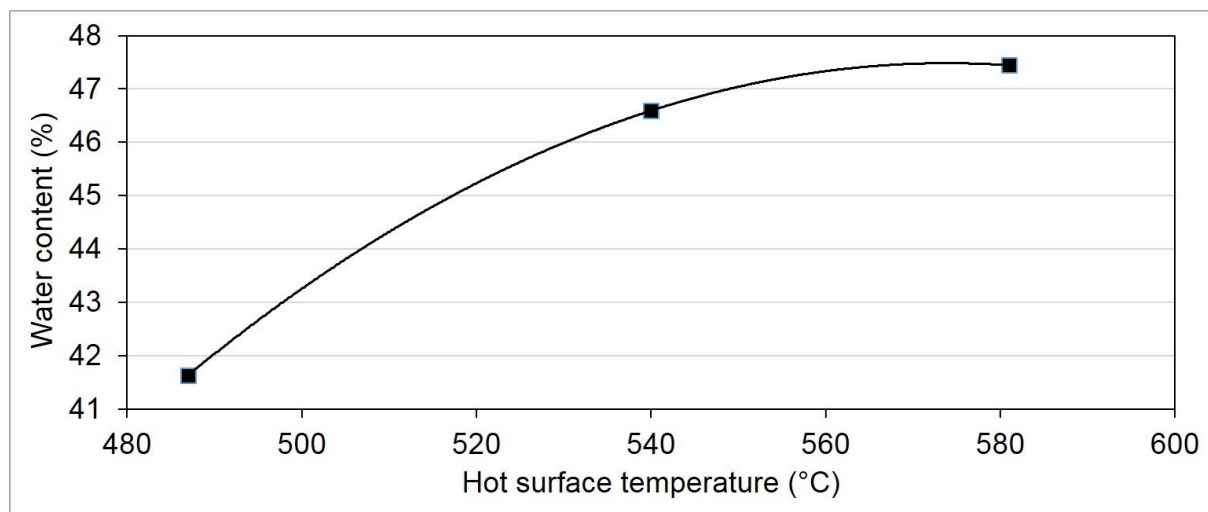


Figure 12: Water mass fraction as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

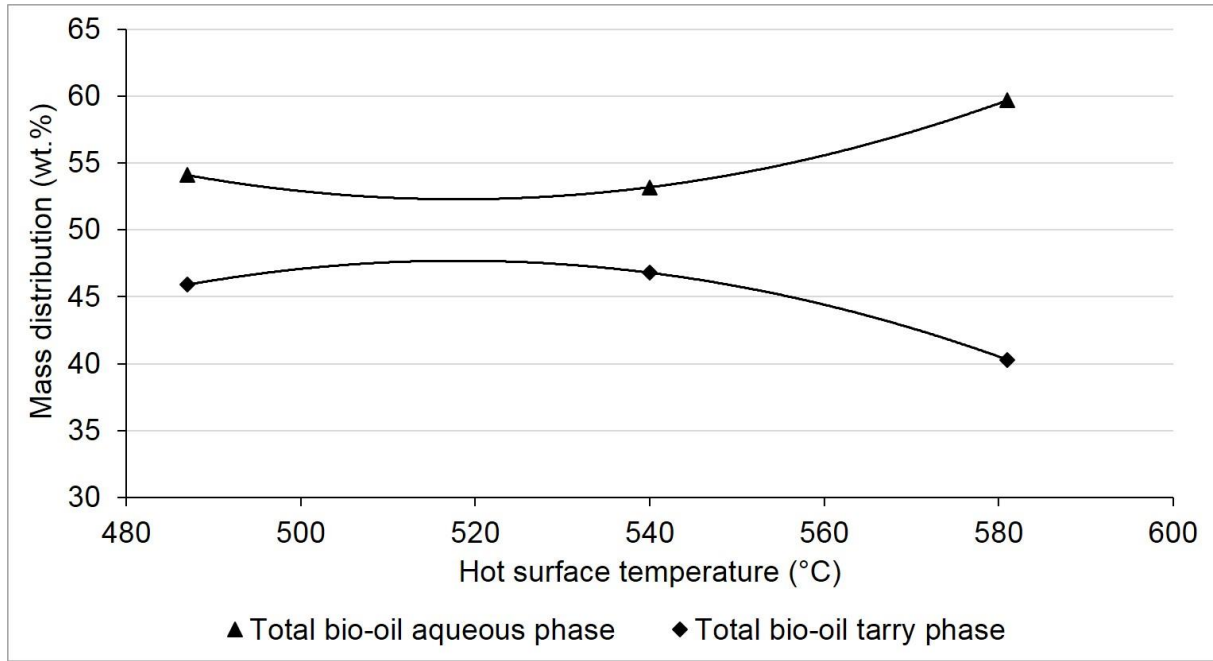


Figure 13: Phase separation into aqueous and tarry phase as function of hot surface temperature for wheat/barley straw (50 bar, 133 rpm)

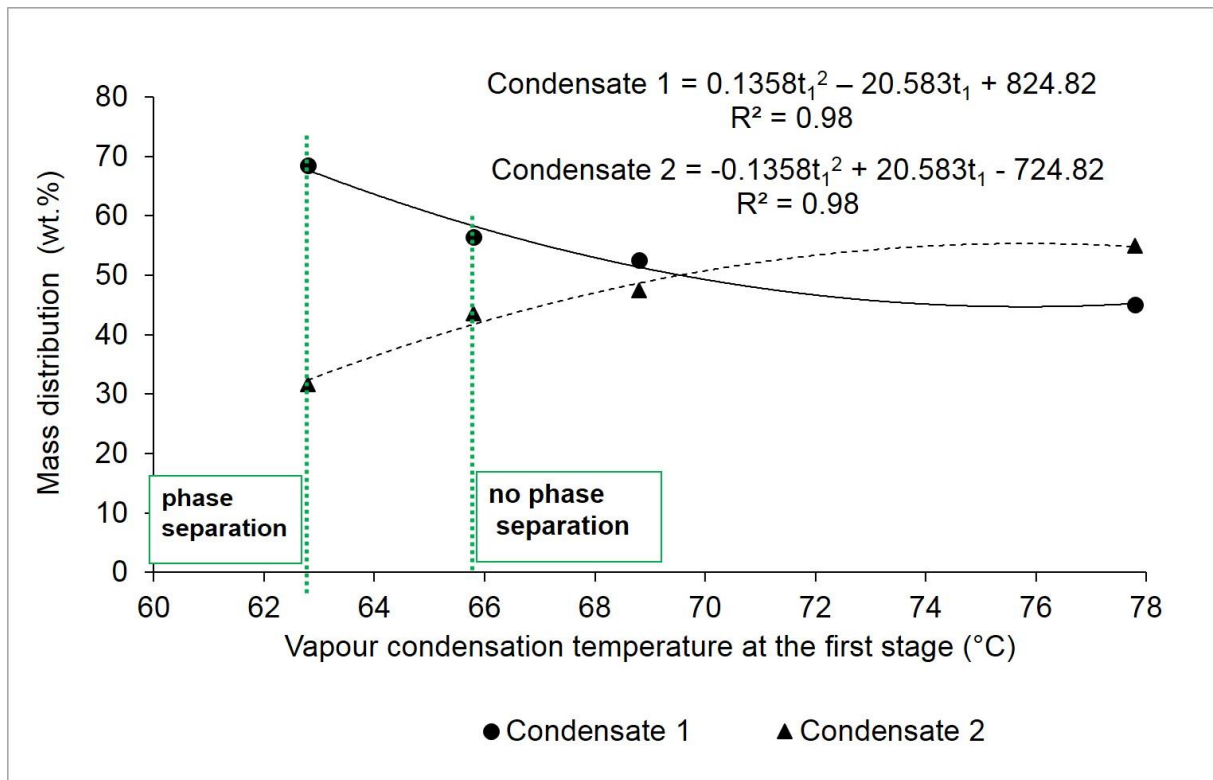


Figure 14: Liquid yields in first and second stage as function of first condenser operating temperature for wheat/barley straw (540 °C, 50 bar, 80 rpm)

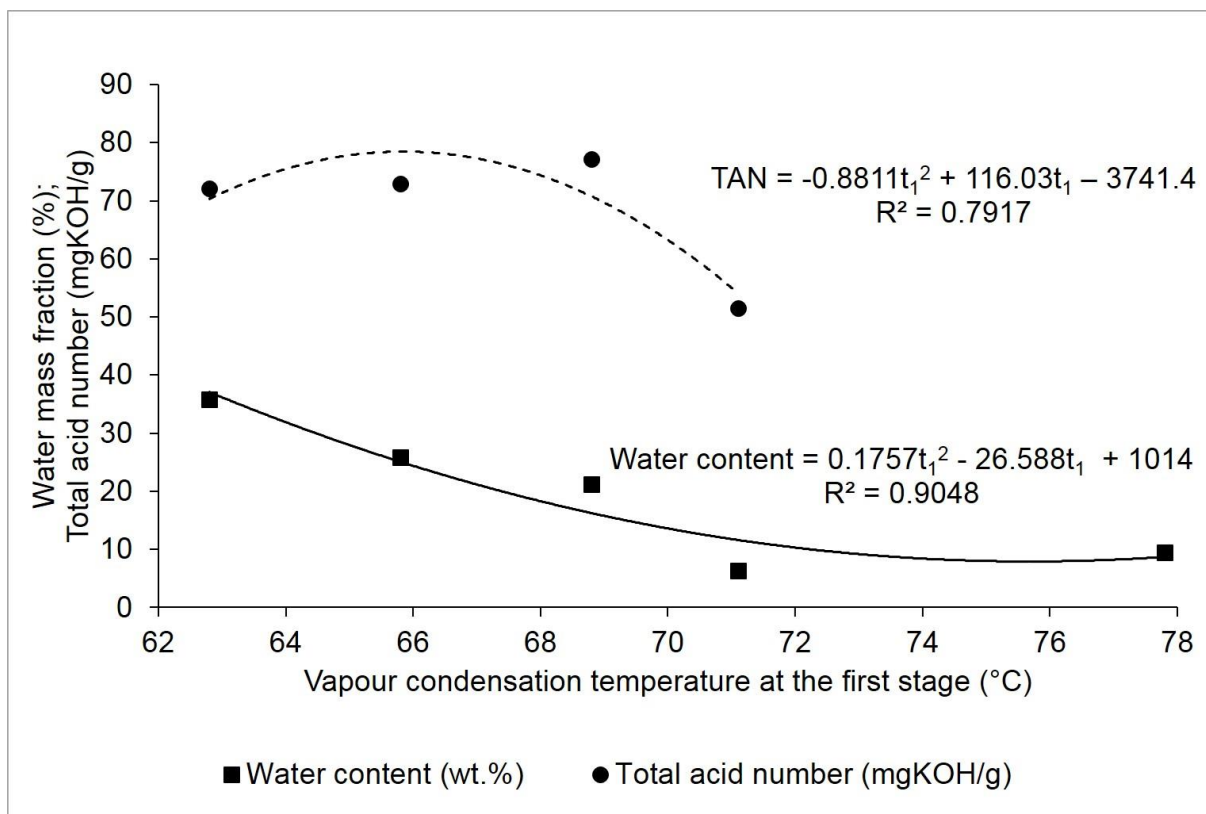


Figure 15: Water mass fraction and total acid number of liquid product in first stage as function of first condenser operating temperature for wheat/barley straw (540 °C, 50 bar, 80 rpm)

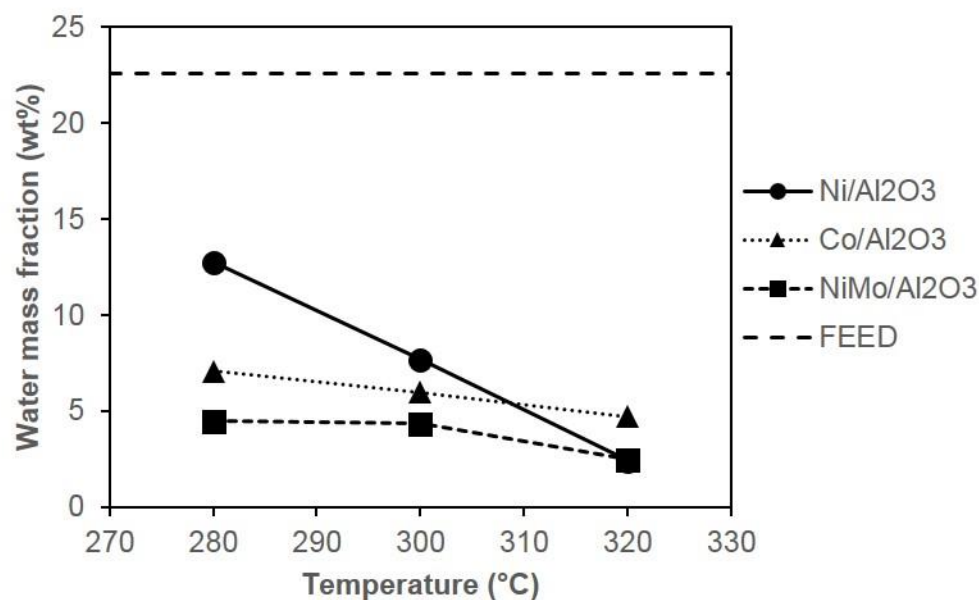


Figure 16: Water mass fraction as function of reaction temperature for mild hydrotreatment

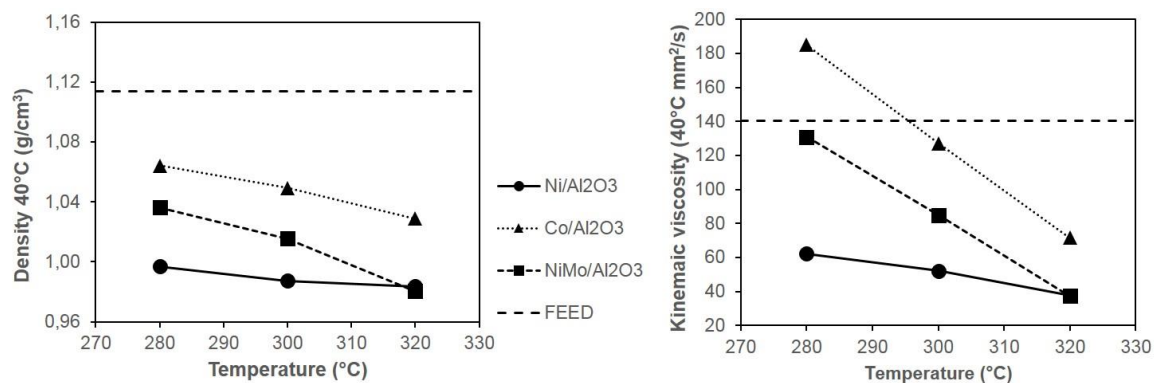


Figure 17: Density and kinematic viscosity as function of reaction temperature for mild hydrotreatment

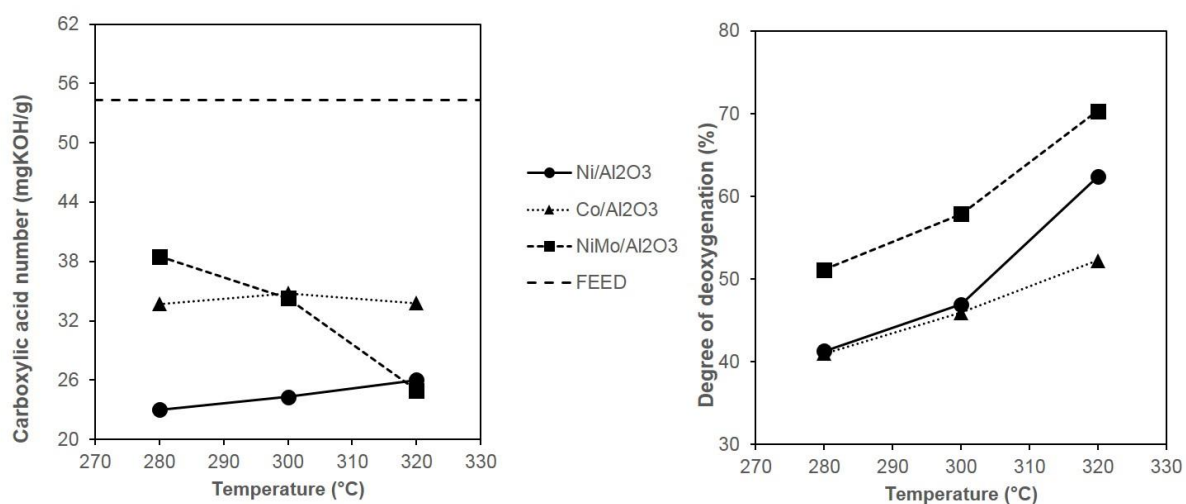


Figure 18: Carboxylic acid number and Degree of deoxygenation as function of reaction temperature for mild hydrotreatment

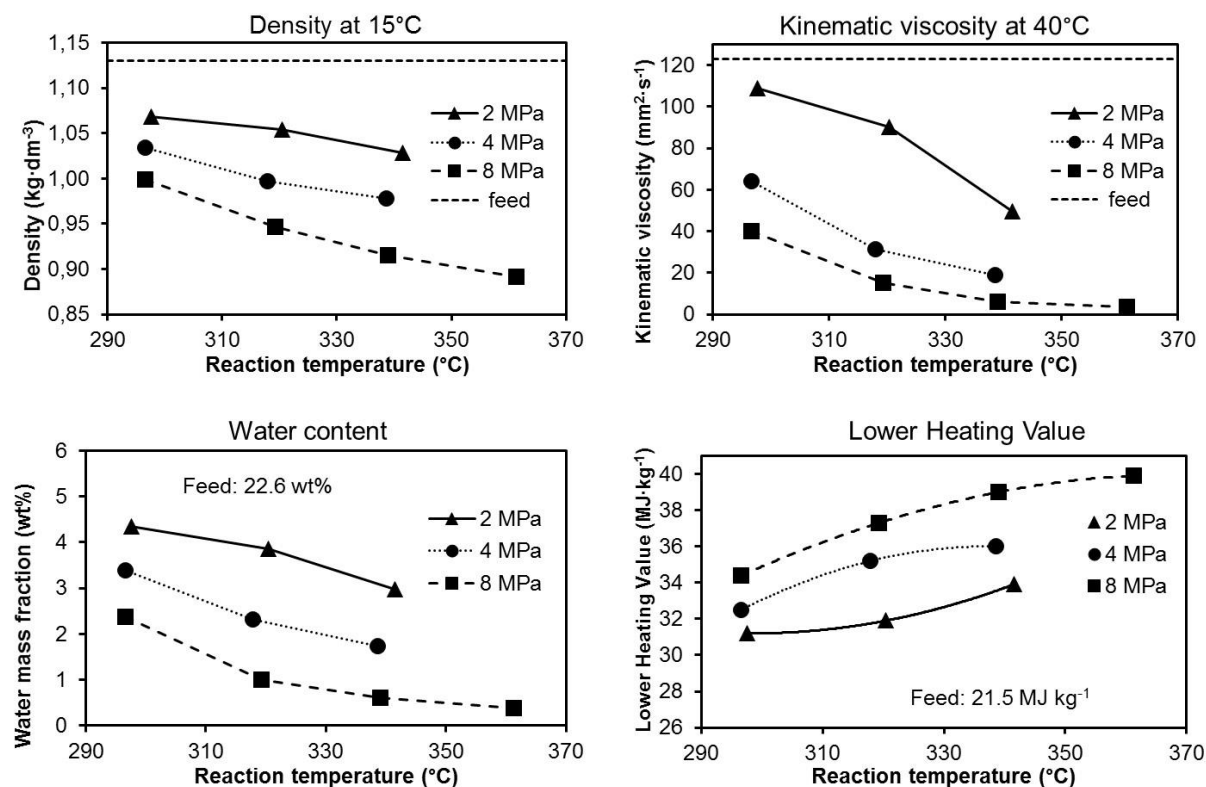


Figure 19: Results of extended testing with commercial NiMo-catalyst (sulphidized)

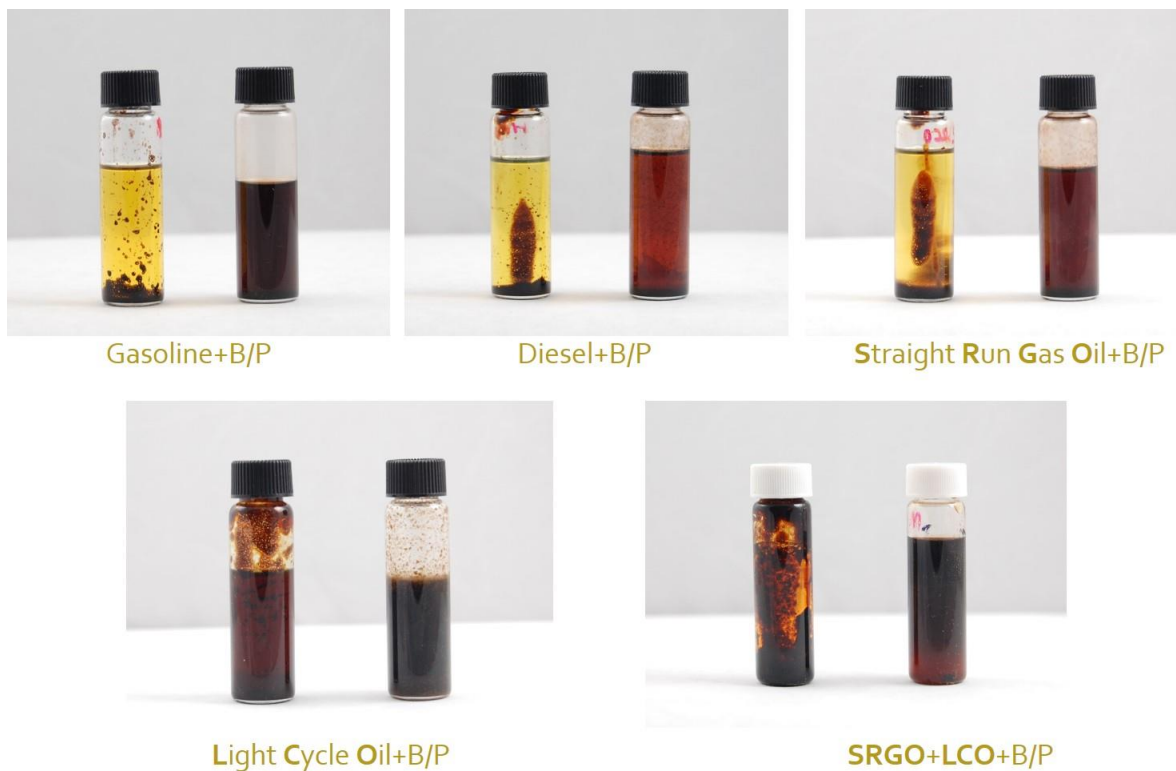


Figure 20: Miscibility tests with typical liquids from refineries with raw bio-oil (B, left) and organic product from mild hydrotreatment (P, right)

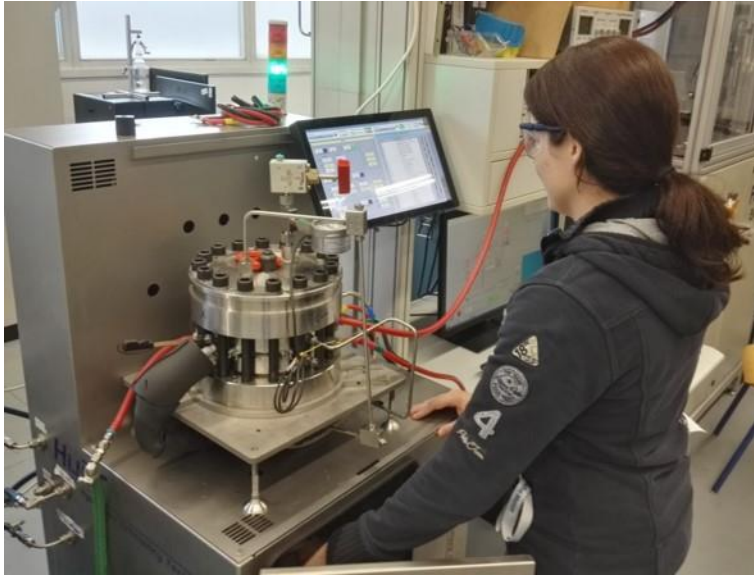


Figure 21: Multiple cell test system for hydrogen compression and purification