Upgrading of Fast Pyrolysis Condensates via Esterification with Higher Alcohols

Tim Schulzke\textsuperscript{a*}, Stefan Conrad\textsuperscript{a}, Stefan Kaluza\textsuperscript{a}, Tom Van Loo\textsuperscript{a}

\textsuperscript{a}Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Osterfelder Strasse 3, 46047 Oberhausen, Germany

corresponding author: tim.schulzke@umsicht.fraunhofer.de, tel. +49 208 8598-1155, fax +49 208 8598-221155

Access to published version: \url{http://dx.doi.org/10.1016/j.biombioe.2017.05.010}

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**Abstract**

The utilization of fast pyrolysis condensates is hindered by unwanted properties like corrosivity, high viscosity and tendency to polymerization. These characteristics result from the high content of organic acids and multiple functional groups and C-C double bonds. As an alternative to severe hydroprocessing, the addition of alcohol and subsequent esterification of acids and acetalization of aldehydes is investigated. Pyrolysis condensates are mixed with butanol and an acidic catalyst is added. This mixture is heated and kept under reflux in a dean-stark-apparatus to continuously boil off the water. As reference homogeneous liquid acids are used and compared to solid acid catalysts like ZnO or zeolites. The advantage of the heterogeneous, solid catalysts is the possibility to remove the solids after reaction and use them again for another batch in contrast to the homogeneous acids, which remain in the solution and need to be neutralized at the end. The most promising catalyst candidates are then used in experiments with varying process parameters. All products are analyzed for total acid number, water mass fraction, dynamic viscosity and higher heating value. The total acid number can be reduced by 90 % (from 110 to below 10 mg g\textsuperscript{-1}), the water mass fraction by 90 % (from 25 % to below 2 %), the viscosity by 70 % (from 18 to 5 mm\textsuperscript{2} s\textsuperscript{-1}) and the higher heating value can be increased by 45 % (from 16.6 to 31 MJ kg\textsuperscript{-1}). These improvements should allow the utilization of upgraded pyrolysis liquids in standard boilers and as fuel in CHP plants.
Keywords: ablative fast pyrolysis, pyrolysis oil upgrade, esterification, total acid number (TAN)

1 Introduction

Ablative fast pyrolysis has the potential to produce liquid energy carrier from abundantly available [1], residual solid biomass like cereal or rape straw under economic conditions [2, 3]. Although pyrolysis condensates as primary products are a mixture of high-value compounds, they exhibit several disadvantageous properties [4, 5]:

- high water content resulting in low heating value (compared to fossil fuel) [6],
- high oxygen content in the compounds, again resulting in low heating value [7],
- low pH-value due to high organic acid content and thus high corrosivity,
- increasing viscosity over storage time due to high reactivity of constituents,
- immiscibility with gasoline, diesel and biodiesel.

Subsequent distillation of the total condensates as usual in mineral oil refineries to separate liquid constituents according to their boiling point is only possible to a very limited extent, because highly reactive organic compounds tend to polymerize (acid catalyzed condensation polymerization) to higher molecular weight compounds under the influence of heat and thus remain as a polymerized, coked bottom residue [8-10]. Only the removal of water and organic acids (mainly acetic acid) together with a restricted amount of other low boiling components would be possible [8, 10]. Other reports show that only 35 – 50 % of the starting material can be separated by a distillation under atmospheric pressure [11]. Wang was able to show that with a molecular distillation a separation of 85 % could be achieved without coking or polymerization [12]. However, the implementation is lengthy and the equipment expensive. Next to distillation methods, extracting and chromatographic methods are reported in the literature as well [13], but these are also either expensive or energy consuming.

Usual upgrade technologies of catalytic cracking over zeolites or deep hydrogenation aim at more or less complete removal of oxygen from the molecules to produce hydrocarbons, which are then miscible with diesel fuel [4]. Both technologies are expensive and only economically realizable in large scale, which somehow thwarts the approach of cheap first conversion step from biomass to liquid intermediate product. Catalytic cracking is a process used in refinery with very high amount of circulating catalyst, because catalyst lifetime is in the range of some minutes due to severe coking and needs early regeneration in a separate reactor. This leads to large and expensive equipment. Hydrotreating as alternative has a high hydrogen demand, due to chemical equilibrium needs high hydrogen overspill and thus large gaseous recycle, operates under high pressure and elevated temperatures and usually uses expensive precious metal catalysts [4].
A different approach would avoid complete oxygen removal, but still aim to greatly improve liquid properties.

The main idea would be to chemically mask the catalytically active and most reactive functional groups to reduce the polarity of the compounds, thus reducing their water solving capacity, and significantly decrease acidity and thereby corrosivity. This would lead to a liquid fuel with lower water content and a medium heating value, that might be applicable as substitute of heavy fuel oil.

2 Theory

The most reactive compounds, which are present in pyrolysis condensates, are aldehydes, ketones and nonaromatic acids. The acids cause the high corrosivity of the liquids and together with aldehydes and ketones they are mainly responsible for the aging behavior, which leads due to polymerization reactions to increasing molecular weight and thus increasing viscosity. A stabilization of the pyrolysis condensates can be reached by either removing these components or masking the functional groups. The removal of these compounds from the mixture is laborious on one hand and on the other withdraws the noticeable heating value. Fortunately the reactive groups of all three families can be masked with the same reactant, namely alcohol [14-16].

Figure 1: Reaction schemes of ketalization/acetalization (upper row) and esterification (lower row)

Figure 1 depicts the reaction schemes, which are both catalyzed by acids. For nonaromatic acids an equimolar amount of alcohol is necessary, while for the full conversion of ketones and aldehydes ($X^2 = H$) two molecules of alcohol per ketone/aldehyde are consumed. In both reactions an equimolar amount of water is produced and they are reversible under the same reaction conditions leading to an equilibrium composition. This chemical equilibrium is strongly influenced by the initial amount of water in the pyrolysis condensate and the fate of water during reaction. If water can be removed constantly from the reaction mixture the chemical equilibrium of the reactions can be shifted to the product side of much less reactive ketics, acetals and esters as desired. This effect can be achieved, if the reaction is conducted under reflux and the evaporated mixture of water and alcohol exhibits a miscibility gap in condensed state. The lowest boiling alcohol, which is almost immiscible with water, is butanol. With the use of such higher alcohol that is immiscible with water it becomes possible to separate them both after condensation to return the alcohol to the reactor and permanently remove the water from the mixture. By means of this approach which is close to reactive distillation it would be possible to drive the esterification and ketalization/acetalization reactions to full conversion in theory.

3 Methods and Materials

3.1 Production of pyrolysis condensates
The condensates from ablative fast pyrolysis were produced in a laboratory plant delivered by PyTrade GmbH, Hamburg. Figure 2 shows a process block diagram (a) and a photograph (b) of this small plant.

Figure 2: Laboratory ablative fast pyrolysis plant, a) block diagram, b) photograph

The biomass in cylindrical shape with a diameter of 50 mm is fed from the right side with hydraulic pistons with a nominal throughput of 10 kg h\(^{-1}\) and pressed against the electrically heated, rotating surface (shown in the center of the picture, pulled out of the reactor housing). At the contact surface the biomass rapidly heats up and reacts to the primary products: char and pyrolysis vapors. The coarse char follows gravity and is collected in a catch pot below the reactor. Fine char and ash particles are carried out of the reactor with the flow of gas and vapor. These fines are separated from the gas flow with means of a cyclone, which is integrated in the reactor insulation. Reactor, cyclone and piping are equipped with electrical trace heating operated at 450 °C to avoid condensation of pyrolysis liquids prior to the condenser. The pyrolysis vapor is cooled and condensed in a double effect cooler equipped with a cooling jacket and internal cooling coil, both operated with cooling water at around 15 °C. The non-condensable gases together with the pyrolysis condensates enter into the box-shaped catch tank below the cooler, where the droplets are separated and collected. Remaining aerosols are removed from the permanent gases in a subsequent electrostatic precipitator (ESP), which runs at a voltage of about 14 kV. As the ESP is mounted on top of the catch tank, the collected aerosols flow down and are combined with the previously separated condensates. The permanent gases which contain nitrogen from inertization and CO\(_2\), but also carbon monoxide, hydrogen and methane, as main constituents are fed to a thermal post-combustion and then released to atmosphere. The overall yields of primary products from the pyrolysis are solids 18.4 % and 31.6 %, liquids 59.9 % and 49.6 % and permanent gases 10.8 % and 11.6 % for beech wood and straw mixture, respectively. The error in mass balance closure is 10.9 % for beech wood and 7.2 % for straw mixture. [8, 9]

The condensates from several test runs were jointly collected in the catch tank to receive a condensate with representative average composition. Solid rods of beech wood and a briquetted mixture of wheat and barley straw with a mass fraction of 50 % each were used as feedstock. The liquid produced from beech wood was single phase, while the condensates produced from straw underwent instantaneous phase separation to give an aqueous phase and a heavy, viscous tarry phase below the aqueous phase. The condensates were filled into canisters (both phases produced from straw separately) and stored at 2 °C in a refrigerator to avoid aging between condensate production and esterification experiment. By this method all esterification experiments could be performed using the same batch of pyrolysis condensates per respective biomass feedstock, whereof the majority of experiments was conducted with condensate produced from beech wood.
Table 1 shows the composition of the pyrolysis condensates from beech wood and the two phases from cereal straw as analyzed by Thünen-Institute for Wood Research in Hamburg, Germany.

Table 1: Lumped composition of pyrolysis condensates from beech wood and cereal straw

3.2 Experimental setup for esterification
The experiments were conducted in a 250 cm$^3$, 3-neck round-bottom flask equipped with magnetic stir bar, thermometer and a Dean-Stark apparatus with reflux condenser on top. The flask was immersed in an oil bath with temperature control. The left part of Figure 3 shows the overall experimental setup. Pyrolysis condensate and alcohol together amounted to 160 cm$^3$ in every experiment, while the individual amount was varied. The majority of experiments was conducted with equal amounts of 80 cm$^3$ each. Butanol and ethanol were used in analytical grade (Sigma Aldrich). Also a mixture of higher alcohols produced from ethanol [17] with the main components being butanol and hexanol was used. For each experiment 5 g of varying catalysts were added. The mixture was heated up to the desired reaction temperature between 80 °C and 120 °C and kept at this temperature for 6 hours to make sure that no additional water could be caught in the burette of the Dean-Stark apparatus (see Figure 3, right side). While most of the experiments were conducted with ambient air above the reaction mixture, some experiments had a small nitrogen flow through the flask, to remove oxygen from the gas hold-up.

Figure 3: Experimental setup (left) and detailed view on burette part of Dean-Stark apparatus (right)
A similar setup for reactive distillation was used by Mahfud [14], but in his experiments he applied low absolute pressure at around 5 kPa to keep the reaction temperature as low as possible (about 60 °C). In this work, higher temperatures and atmospheric pressure were used.
As ethanol and water do not separate in the Dean-Stark apparatus the experimental procedure was different. The reaction mixture was boiled under reflux for 6 hours. On the second day a distillation with maximum temperature of 120 °C was performed as attempt to remove the water.

3.3 Analytical methods applied
The biomass feedstock was analyzed for water and ash content following DIN EN 14774-2 [18] and DIN EN 14775 [19] respectively, elemental composition (C, H and N using an elemental analyzer from elementar, S and Cl from the condensate of the bomb calorimeter test for heating value determination, Na and K aqua regia dissolution of biomass ash followed by ICP-AES; O by difference) and heating value following DIN 51900 [20]. The pyrolysis condensates were analyzed for elemental composition (C, H, N, S; O by difference), kinematic
viscosity using an Ubbelohde viscosimeter, water mass fraction (Karl-Fischer titration), density, heating value
and total acid number (TAN), using an automated titrator following ASTM D 664 [21]. Samples of the two
different pyrolysis condensates were sent to Thuenen-Institute for Wood Research (TI), Hamburg, for full GC-
MS/FID analysis. The products form esterification underwent the same analytical methods as the pyrolysis
condensates, but only selected samples were sent to TI for GC analysis. Only in case of heterogeneous catalysts
these were removed prior to analysis via filtration. The homogeneous catalysts remained in the product mixture
and were not neutralized.

4 Results

4.1 Catalyst Screening

A first set of experiments was conducted to screen different types of catalysts to identify the most promising one
for more detailed examination. For this set of experiments always 60 cm$^3$ of pyrolysis condensate produced from
beech wood was mixed with 100 cm$^3$ butanol and 5 g of catalyst. The resulting kinematic viscosity at 40 °C,
water mass fraction and TAN are shown in Figures 4 to 6, respectively. For comparison, the respective original
values of the untreated pyrolysis condensate are given as well as values for blind tests (values of reaction
mixture without catalyst prior to reaction to show dilution effect of alcohol addition) and autocatalyzed
experiments (reactions performed without addition of acid catalyst to show initial catalytic effect of carboxylic
acids present in pyrolysis condensate). Two homogeneous liquid acids were used: sulfuric acid H$_2$SO$_4$ and p-
toluene sulfonic acid (PTSA). The majority of applied catalysts were heterogeneous solid acids like ZnO,
polystyrene resin bearing sulfonic acid groups (Amberlyst™) and several zeolites.

Simply mixing the pyrolysis condensate with a nearly equal amount of butanol on mass basis (100 cm$^3$ butanol
correspond to 81 g, while 60 cm$^3$ pyrolysis condensate weigh 72 g) naturally reduces the water mass fraction by
half (see Figure 5). At the end of the experimental procedure with constant water removal, an average water
mass fraction of about 5% remains with relatively small variation. The lowest viscosity is observed for the blind
test due to dilution effect. During reaction, water is removed and the average molecular weight increases due to
esterification and acetalization/ketalization (see Figure 4). As there is again only small variation in final viscosity
there is no clear preferential catalyst to be selected form this property.
From stability point of view and corrosion behavior TAN is the most crucial parameter of the pyrolysis liquid. Many of the screened catalysts don’t exhibit large improvement in TAN (see Figure 6), although some water was removed. Only the two homogeneous acids and Amberlyst™ show a significant reduction in TAN during the reaction compared to the blind test. The TAN values as KOH consumption for the experiments performed with PTSA and H₂SO₄ are dominated by the remaining strong acids in the product mixture, as they could not be removed and were not neutralized. Accounting for that the values would lie in a similar range as with Amberlyst™ of around or even below 10 mg g⁻¹ compared to 113.5 mg g⁻¹ for the pure condensate produced from beech wood. The analysis of pore diameters of the solid catalysts revealed that for some of them they might be too small for the large organic molecules to reach the acidic surface within the pores as the size of the pores of zeolites is 6 Å to 7 Å, while the pore size of the Amberlyst™ resin is in the range of 220 Å. On the other hand, strong acidity seems also necessary for an effective conversion as can be deduced from the experiment with ZnO. Although the average pore size is about 700 Å and thus doesn’t hinder access of molecules to the inner surface, the acidity seems to be not sufficient due to the amphoteric nature of ZnO. From these results catalysts from the Amberlyst™ group were chosen as the most promising candidates for all further experiments.

The mass balance for water was drawn up for all experiments. For Amberlyst™ the terms become as follows. 60 cm³ pyrolysis condensate from beech wood had a weight of 70.93 g. The mass fraction of water contained in the pyrolysis condensate was 25.8 % (see Table 1), which gives a total amount of water in the original pyrolysis condensate fed to the flask of 18.3 g. During the experiment 21.0 g of water were collected in the Dean-Stark-apparatus (see Figure 3) and the final product contained 4.16 g of water, as the final product had a weight of 129.86 g and a water mass fraction of 3.2 %. These two values together give a total amount of water after reaction of 25.16 g. This means that 83.5 % of the total water could be removed from the final product during the experiment and 6.86 g of water result from reactions. If all organic acids, aldehydes and ketones, which were identified in the GS-MS analysis of the pyrolysis condensate carried out by Thuenen-Institute for Wood Research in Hamburg, are accounted for, a maximum amount of 4.16 g of water could be produced by full conversion. This indicates that also phenols and sugars must react with the alcohol to form some ether-like products, as alcohols themselves were only present in a negligible amount of 0.04 % in pyrolysis condensate (see Table 1). These reactions must contribute to water production even more significant, as TAN of the final product indicate the presence of remaining acidic groups. Esterification and acetalization/ketalization seem to be faster than the polymerization reactions or these are suppressed in presence of alcohols, although polymerization reactions usually take place roughly at the same temperature as esterification (compare experience with atmospheric distillation of untreated pyrolysis condensate...
which gives large amount of polymerized solid residue after distillation up to 180 °C). Homogeneous catalysts like p-toluene sulfonic acid should be better for a complete conversion of carboxylic acids and aldehydes/ketones, because no steric hindrance due to restricted pore sizes occurs in comparison to heterogeneous catalysts. But under the investigated conditions no clear advantage was visible in the catalyst screening. On the other hand, heterogeneous catalysts have the clear advantage, that they can be separated from the product liquid with simple filtering and reused for further conversion. Also, the homogeneous catalysts must be neutralized in the liquid, which gives rise to salt content that might impede some later applications and introduce other unwanted elements, if amines are used for instance. These facts combined clearly favor the heterogeneous catalysts, of which Amberlyst™ type candidates proved to be the most promising ones. The overall results compare quite well with the findings of Mahfud [14]: in his experiments with beech wood derived pyrolysis condensates he could reduce the water mass fraction to around 9 % and increase the higher heating value to 28.7 MJ kg\(^{-1}\) on dry basis. Besides sulfuric acid he applied also a solid acid catalyst: Nafion™. This catalyst is very similar to the chosen candidate in this work as both solids are sulfonated polymers. Nafion™ has a backbone from polytetrafluoroethylene while Amberlyst™ has a backbone from polystyrene. The catalytically active groups are added sulfonic acid groups in both cases. The main progress in this work is the applied higher working pressure (ambient pressure instead of vacuum around 5 kPa absolute pressure).

4.2 Upgrading of pyrolysis oil produced from beech wood and cereal straw

After the identification of the most promising catalyst family a set of experiments was conducted with various ratios of pyrolysis condensates from beech wood and butanol, because mixtures with nearly equal amounts on mass basis of butanol compared to pyrolysis condensates would be very uneconomical as butanol is relatively expensive and larger amounts stand for a large overspill of alcohol. The overspill ratio of a mixture with equal amounts (80 cm\(^3\) each) was estimated to be around 1.7, based on the analyzed content of acids, aldehydes and ketones in the pyrolysis condensates. The catalyst used for this test series was Amberlyst36™, which has slightly lower acidity compared to the one used in catalyst screening and a lower maximum temperature, but the same overall structure with regard to backbone resin and kind of active sulfonic acid groups. This change in catalyst had to be done, because Amberlyst70™ was no longer available in small amounts needed for laboratory experiments. The liquid volume was fixed to 160 cm\(^3\), while the amount of pyrolysis condensate was varied from 40 to 120 cm\(^3\) in steps of 20 cm\(^3\). The overspill ratio of butanol for these mixtures is approximately 5.1, 2.83, 1.7, 0.98 and 0.57, respectively.

Figure 7: Kinematic viscosity at 40 °C, obtained for butanol-pyrolysis condensate ratios
Figures 7 to 9 show the results for viscosity, water mass fraction and TAN, respectively. The value for blind experiment is for a mixture of 100 cm$^3$ butanol and 60 cm$^3$ pyrolysis condensate. While kinematic viscosity and TAN of the reaction product increase with decreasing initial butanol amount (mainly due to decreasing dilution effects), the water mass fraction shows a minimum value at a mixture with equal amounts, although the mixture with 100 cm$^3$ pyrolysis condensate and 60 cm$^3$ butanol is nearly stoichiometric. This effect is not very pronounced as the value for remaining water mass fraction only vary between 1.7 % and 5.7 %, and cannot be explained from first principle.

One experiment was conducted with a mixture of 59 cm$^3$ aqueous phase and 21 cm$^3$ tarry phase of condensates from straw pyrolysis (to mimic the overall weight composition of the two phase condensate) together with 80 cm$^3$ butanol and 5 g Amberlyst36™ as catalyst. The resulting single phase reaction product showed a kinematic viscosity at 40 °C of 4.5 mm$^2$ s$^{-1}$, a water mass fraction of 2.7 % and a TAN value as KOH of 49.3 mg g$^{-1}$. These values are quite similar compared to experiments with pyrolysis condensates from beech wood. But evaporation of water/alcohol and reaction only occurred, if a small nitrogen flow was led through the flask.

To further investigate only the upgrading of the tarry phase from straw pyrolysis, which already has lower TAN and higher HHV (higher heating value) compared to the overall mixture and also compared to condensates derived from beech wood pyrolysis, 5 experiments with the same conditions (80 cm$^3$ butanol, 80 cm$^3$ tarry phase, 5 g Amberlyst36™) were conducted under a small nitrogen flow through the flask. The resulting values are given in Table 2. The values show good reproducibility, especially for water mass fraction, HHV and TAN. The mean values and standard deviations are: water mass fraction (2.56±0.36) %, TAN as KOH (38.94±3.6) mg g$^{-1}$, higher heating value (31.48±0.19) MJ kg$^{-1}$ and kinematic viscosity (10.3±3.15) mm$^2$ s$^{-1}$. Unfortunately, the reduction in TAN through the reaction is not as pronounced as expected.

Table 2: Results for upgrading of tarry phase from straw pyrolysis

The possible reason for high remaining TAN value, although a large amount of water originating from reaction can be calculated, is the occurrence of catalyst attrition due to intense contact of the magnetic stir bar with the catalyst particles during the 6 hours of experiment. The attrited catalyst particles pass through the filter, which separates the product solution from the heterogeneous catalyst, and their acidic groups pretend a higher TAN in the product. To confirm this theory, an experiment with pyrolysis condensate from beech wood was performed with the same conditions, but with the catalyst Amberlyst36™ contained within a nylon bag to prevent catalyst attrition. The water mass fraction in this experiment was 1.3 % compared to the standard experiment with 4.4 %.
The TAN value as KOH was 50.7 mg g\textsuperscript{-1}, compared to 53.7 mg g\textsuperscript{-1} in the similar standard experiment. This difference seems to be quite small. But the calculated amount of reaction water was only 2.8 cm\textsuperscript{3} for the experiment with catalyst contained in a bag, while it was 6.1 cm\textsuperscript{3} for the standard conditions. This shows that less than half of the conversion occurred compared to the reference experiment (because the catalyst is not so well mixed with the reaction solution), but the remaining TAN value at the end of the reaction is lower than in the reference experiments. This certifies the idea of either reducing mechanical stress to the catalyst or developing a similar solid catalyst with more rigid backbone structure compared to the polystyrene resin.

### 4.3 Comparison of esterification with different alcohols

As butanol is an expensive raw material, it would be interesting to use a cheaper alternative. Bio-Ethanol produced from starch or sugar would represent such a feedstock. It is a smaller molecule and therefore should react faster with the pyrolysis components. As described in paragraph 3.2 the experimental procedure was different due to the unlimited miscibility of ethanol with water. The evaporating azeotropic mixture contains 95 % ethanol and only a small amount of water. As no phase separation occurs in the condensed liquid, all the water present in the pyrolysis condensate together with the evolving reaction water remain in the reaction mixture, thus limiting the conversion due to chemical equilibrium. The distillation performed on the second day removes the ethanol overspill (which could be used for further batches and is therefore advantageous in principle) together with the water at temperatures similar to the reaction. Unfortunately, the majority of the ethanol leaves the liquid prior to water evaporation. Therefore, the reverse reaction is favored, which leads to decomposition of esters and acetal/ketals. The resulting liquid shows even worse properties than the blind sample of a mixture of pyrolysis condensate and ethanol. Definitely the chosen experimental procedure was inappropriate. A better approach described by Sundqvist \[15\] first removes the water from the raw pyrolysis condensate by means of azeotropic distillation with an entrainer like petroleum ether as much as possible and performs esterification afterwards and leaving the reaction water in the resulting product.

An alternative approach is to combine the advantages of ethanol as cheaper reactant derived from biomass on one side and immiscibility of higher alcohols with water on the other side by separately converting ethanol to a mixture of higher alcohols \[17\]. For 4 experiments such a mixture was used. It was mainly composed from n-butanol, 2-ethyl-butan-1-ol and n-hexanol (see Figure 10). 80 cm\textsuperscript{3} pyrolysis condensates from beech wood were mixed with 80 cm\textsuperscript{3} of this mixture of ethanol-derived higher alcohols together with 5 g Amberlyst36™ as catalyst. Reaction and evaporation only occurred under a small flow of nitrogen through the flask.
Table 3: Results for upgrading of pyrolysis condensates from beech wood with ethanol-derived higher alcohols

The resulting values are given in Table 3. Again, good reproducibility is obvious from the values. The mean values and standard deviations are: water mass fraction (1.73±0.25) %, TAN as KOH (46.9±4.86) mg g⁻¹, higher heating value (32.19±0.35) MJ kg⁻¹ and kinematic viscosity (29.35±5.49) mm² s⁻¹. The TAN values are in the same range as achieved with pure butanol. These results were attained with standard setup, so the catalyst was not protected against attrition. Therefore, the TAN value of completely catalyst-free product mixture is assumed to be even lower.

The future work on this topic will focus on the development of heterogeneous solid acid catalysts with improved mechanical stability and improvement of process conditions. The resulting liquid energy carriers will be examined with regard to their potential field of application: unmodified heavy fuel burners or ship’s engines.

6 Conclusions

The conversion of pyrolysis condensates from beech wood as well as cereal straw with alcohols is a promising upgrade option to improve their properties by greatly reducing TAN and thereby corrosivity. This would open up a more widespread application of such upgraded liquids as direct replacement of heavy fuel oil, because the fuel tanks and burner systems potentially don’t need to be modified. Also miscibility with standard fuels might improve, as water mass fraction is greatly reduced and polarity of compounds decreased. Both hypotheses will be confirmed in future research.

For practical reasons heterogeneous catalysts for the esterification reaction are more favorable than homogenous as they can easily be removed after reaction and reused. During intense catalyst screening the Amberlyst™ family of catalysts was identified to be the most suitable, resulting in low water content and lowest TAN. Under reaction conditions—atmospheric pressure and temperatures between 80 °C and 120 °C—water as well as alcohol evaporated from the reactor in reactive distillation. Only higher alcohols starting with butanol show a miscibility gap with water, which enables easy separation of water and alcohol in condensed phase downstream the reactor. The alcohol can then be re-fed to the reactor while the water is constantly removed.

Variation of butanol-pyrolysis condensate ratio revealed an optimal proportion in the range of equal volumes, which represents a stoichiometric ratio of 1.7. Although direct use of ethanol was not successful due to its miscibility with water, it can be converted to higher alcohols and experiments performed with such a mixture where as successful as the ones with pure butanol.

The condensates of pyrolysis vapors derived from beech wood and cereal straw are quite different. While condensates from beech wood pyrolysis are single phase liquids, condensate from cereal straw pyrolysis
instantaneously undergo phase separation. But after esterification reaction with the same amount of butanol the resulting liquids are very similar as they are both single phase and have comparable TAN values as KOH consumption of 41.5 mg g$^{-1}$ and 49.3 mg g$^{-1}$.

7 Acknowledgements

The presented work are results from the project “Development of a combined process for the upgrading of pyrolysis oil with biogenic alcohols and hydrogen”, which is funded by the Federal Ministry of Food and Agriculture through its funding agency FNR e.V. under the grant number 22018811 by decision of the German Bundestag.

8 References


Table 1: Lumped composition of pyrolysis condensates from beech wood and cereal straw

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*not detected

Table 2: Results for upgrading of tarry phase from straw pyrolysis

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<td>14.3</td>
<td>36.1</td>
<td>31.7</td>
</tr>
<tr>
<td>blind</td>
<td>11</td>
<td>6.9</td>
<td>39.8</td>
<td>28.7</td>
</tr>
<tr>
<td>untreated</td>
<td>25.3</td>
<td>nd</td>
<td>70.4</td>
<td>22.8</td>
</tr>
</tbody>
</table>

*not detected, too viscous for used capillary tube

Table 3: Results for upgrading of pyrolysis condensates from beech wood with ethanol-derived higher alcohols

<table>
<thead>
<tr>
<th></th>
<th>water mass fraction (%)</th>
<th>viscosity (mm² s⁻¹)</th>
<th>TAN (mg g⁻¹)</th>
<th>HHV (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amb36-PO-17</td>
<td>1.6</td>
<td>37.5</td>
<td>43.4</td>
<td>32.6</td>
</tr>
<tr>
<td>Amb36-PO-18</td>
<td>2.1</td>
<td>25.8</td>
<td>47.6</td>
<td>32.2</td>
</tr>
<tr>
<td>Amb36-PO-19</td>
<td>1.6</td>
<td>27.7</td>
<td>53.5</td>
<td>32.2</td>
</tr>
<tr>
<td>Amb36-PO-20</td>
<td>1.6</td>
<td>26.4</td>
<td>43.1</td>
<td>31.7</td>
</tr>
<tr>
<td>blind with higher alcohols</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>blind with butanol</td>
<td>16.0</td>
<td>6.2</td>
<td>69.9</td>
<td>23.9</td>
</tr>
<tr>
<td>untreated</td>
<td>25.8</td>
<td>19.7</td>
<td>113.5</td>
<td>16.6</td>
</tr>
</tbody>
</table>

*not determined
Figure 1: Reaction schemes of ketalization/acetalization (upper row) and esterification (lower row)

\[ \text{O} \quad \overset{X^1}{\text{C}} \quad \overset{X^2}{\text{C}} \quad + \quad 2 \text{ROH} \quad \overset{\text{H}^+}{\rightleftharpoons} \quad \overset{X^1}{\text{C}} \quad \overset{\text{OR}}{\text{O}} \quad \overset{\text{OR}}{\text{O}} \quad \overset{X^2}{\text{C}} \quad + \quad \text{H}_2\text{O} \]

\[ \text{O} \quad \overset{\text{X^1 COOH}}{\text{C}} \quad \overset{\text{X^2 COOH}}{\text{C}} \quad + \quad \text{ROH} \quad \overset{\text{H}^+}{\rightleftharpoons} \quad \overset{\text{X^1 COOH}}{\text{C}} \quad \overset{\text{OR}}{\text{O}} \quad \overset{\text{OR}}{\text{O}} \quad \overset{\text{X^2 COOH}}{\text{C}} \quad + \quad \text{H}_2\text{O} \]
Figure 2: Laboratory ablative fast pyrolysis plant, a) block diagram, b) photograph
Figure 3: Experimental setup (left) and detailed view on burette part of Dean-Stark apparatus (right)
Figure 4: Kinematic viscosity at 40 °C, obtained for various catalysts

Figure 5: Final water content, obtained for various catalysts
Figure 6: Total acid number, obtained for various catalysts

Figure 7: Kinematic viscosity at 40 °C, obtained for butanol-pyrolysis condensate ratios
Figure 8: Final water content, obtained for butanol-pyrolysis condensate ratios

Figure 9: Total acid number, obtained for butanol-pyrolysis condensate ratios
Figure 10: Main compounds in mixture of higher alcohols produced from ethanol