Article

Viscosity Reduction of Fast Pyrolysis Bio-Oil by Using CO_2 as an Additive

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Cite This: https://doi.org/10.1021/acs.energyfuels.3c04201

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ABSTRACT: The addition of solvents is an option for reducing the viscosity of fast pyrolysis bio-oil and for slowing down the reaction rate of aging reactions. For this purpose, conventional organic solvents with low molecular mass are deployed, with alcohols in particular. They can determine the costs and overall ecological performance of the final product. In this context, the use of CO_2, which is a side product of pyrolysis, that occurs in the noncondensable pyrolysis gas, can be a favorable option. However, CO_2 has not been used for conditioning of fast pyrolysis bio-oil so far. This work is an evaluation of the influence that pressurized CO_2 as an agent has on the viscosity of fast pyrolysis bio-oil. The utilization of CO_2 can be an asset in the context of further processing steps such as atomization, filtration, or transfer by pumping. The results are compared to the effect of ethanol on the viscosity. It was found that CO_2 at 50 bar leads to a reduction of the original viscosity by 70−80%, as does 5 wt % ethanol in fast pyrolysis bio-oil. In the case of CO_2 usage, there is an approximately linear relationship between the relative viscosity and CO_2 pressure. Furthermore, the temperature dependence of the relative viscosity change for pure fast pyrolysis bio-oil was examined. It reveals Arrhenius-like behavior with a formal activation energy of 66 kJ mol^{-1}. The addition of CO_2 (10 bar) reduces this value to 42 kJ mol^{-1}, while it remains almost unchanged upon the addition of 5 wt % ethanol. The Vogel−Fulcher−Tammann equation was used to describe the temperature dependence but showed no further advantage over the Arrhenius-type equation.
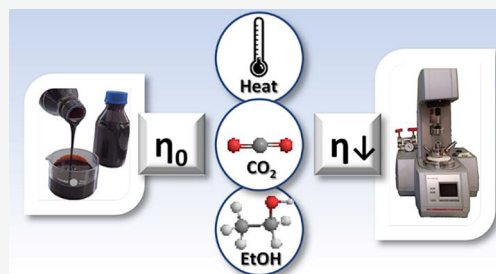
1. INTRODUCTION

Energy production, as it is practiced today, leads to undesirable side products such as CO_2, which in turn promotes global warming. With the rising energy demand expected in the future, the way energy is produced will impact our environment and living conditions.[1] Therefore, switching to other energy sources is necessary, because fossil sources are finite and required to produce commodity chemicals, too.[1] These circumstances demand an alternative carbon-containing resource. The limited options available include chemical recycling of waste materials such as plastics,[2] as well as utilization of carbon dioxide[3] and biomass, which is of particular interest due to its renewable nature.[1,4,5]

A potential way to utilize biomass is the production and use of fast pyrolysis bio-oil (FPBO). It can serve as an intermediate energy carrier for energy and chemical production, and it can make accessible a variety of lignocellulosic biomass feedstocks for associated applications.[1,6] So far, FPBO is exclusively used as a fuel for commercial and industrial burners, as defined in the EN 16900:2017[7] and ASTM D7544-12[8] standards. The technology to produce FPBO from wood biomass is commercially available, inter alia, from Twence/Empyro BV (Netherlands),[9] Fortum (Finland),[10] and Envergent Technologies' RTP (Canada).[11] Other applications, such as the use in Diesel engines, for coprocessing in petrochemical refineries,

or as a feedstock for chemical synthesis are still under development.[10,12]

To establish the utilization of biomass on a large scale across the energy sector, the processing of biogenic waste materials must be considered in order to avoid any competition for resources with the food and feed production sector.[13−16] In using lignocellulosic materials, the largest contributions can be expected from the use of cereal straw and woody biomass derived from agriculture, forestry, and landscaping. For example, the technical potential of cereal straw in Germany is approximately 11−15 Mt/year (dry mass). The amount of woody biomass originating from orchards, vineyards, railway lines, highways, etc., as well as from landscaping amounts to approximately 4.2 Mt/year (dry biomass). Lignocellulosic biomass derived from biodegradable waste, as collected and reported by municipal waste management, and woody biomass originating from public green areas amount to 2.5 Mt/year (dry mass).[16]

A

The pyrolysis process is particularly beneficial for processing biogenic waste, because it has the capability to convert biomass of different qualities and compositions to FPBO.[17,18] The fast pyrolysis process is a thermochemical conversion, which is conducted at atmospheric pressure and typically at around 500 °C in an anoxic atmosphere at short gas residence times of approximately 1 s in the reactor, which requires high heating rates achieved through a carrier material. After a short reaction time, the process is terminated by rapidly cooling the pyrolysis vapors to form FPBO.[18,19] This product consists of water and more than 300 organic substances,[20] and it remains a reactive, occasionally unstable mixture.[21]

Despite the potential advantages of FPBO, its application is currently limited to its use as a source of energy. There is no material use as of now.[7,8] However, considering the diminishing fossil feedstock supply, it is necessary to extend the applications of FPBO. For this purpose, FPBO handling processes need to be improved.[17,22,23] Here, the viscosity is a crucial parameter for characterizing FPBO in general,[7,8] for quantifying FPBO's aging behavior,[21,24,25] and, specifically, for determining its performance when used as a combustion or gasification fuel.[10] Next to the high acidity, which is mainly caused due to the presence of carboxylic acids such as acetic acid (5−10 wt %),[26] the water content (10−30 wt %),[19,20] and other less desirable properties, the high viscosity is a limiting factor for applications.[8,27] However, a number of strategies have been proposed to reduce the viscosity and thus improve the FPBO handling. Recommended measures include preheating of FPBO and the addition of solvents to enhance its fluidity, in order to facilitate its transport to the burner unit and the following atomization for combustion or gasification purposes.[7,8,28]

The viscosity reduction as it occurs during preheating can be determined by temperature-dependent viscosity measurements. The obtained results can be analyzed using an Arrhenius-type equation leading to additional information on FPBO.[29−31] In the work of Nolte and Liberatore,[29] Jampolski et al.,[30] and Oginni and Tingi,[31] the viscosity at different temperatures was measured and the results were used to calculate the formal activation energy with an Arrhenius-type equation. The energy value facilitates a comparison of the fluidities of different FPBOs. We refer to the expression *formal activation energy*, because FPBOs, unlike pure substances, lack an exact molar mass. Furthermore, Oginni and Tingi worked with two additional models (Williams−Landel−Ferry and the power law), indicating that the Arrhenius-type equation is superior to these models with respect to the goodness of fit for the chosen FPBO.[31]

Besides heating, a viscosity reduction can also be achieved by diluting FPBOs with solvents. The resulting dilution effect of some solvents on FPBO has been well described. Frequently used solvents, including alcohols, esters, and ketones, have a low molecular weight. Some of these substances can react with constituents of FPBO. However, the main effect of a viscosity decrease and reduction of aging can be attributed to the dilution with a liquid of low viscosity, which particularly applies to methanol.[32−34]

In the first part, this work explores the viscosity reduction of a wheat-straw-based FPBO through an increase in the temperature. It serves as a reference for the CO_2-based viscosity reduction and as a comparison to other works.[29−31] The results are discussed within the context of an Arrhenius-type equation[35] and the Vogel−Fulcher−Tammann equation

(VFT equation).[36,37] Following the measurements with FPBO only, the same method was applied to FPBO exposed to CO_2 at 10 bar and an FPBO blend containing 5 wt % ethanol.

The second part investigates the viscosity reduction through two solvents. Different concentrations of CO_2 and ethanol are used as solvents here. The measurements with ethanol serve as a reference to put the CO_2 measurements into context, with ethanol being a conventional solvent for FPBO.[7,8]

By reducing the viscosity, solvents improve the FPBO handling by facilitating pipeline transfer (lower pressure drop and thus pumping energy), filtration, and atomization. Moreover, the decision on the appropriate solvents can determine the final cost and environmental performance of products made from FPBOs.

2. MATERIALS AND METHODS

2.1. Fast Pyrolysis Bio-Oil Production. The FPBO used in this study was produced from wheat straw by the bioliq fast pyrolysis pilot plant at the Karlsruhe Institute of Technology. The pyrolysis reaction was conducted at 500 °C and a feed rate of 300−400 kg h^{-1}. Of the two condensates recovered from this plant, only the so-called organic condensate was used, which was obtained during condensation at 85−95 °C.[19] The water-rich aqueous condensate that typically results from the use of ash-rich feedstocks was not considered. Some properties of the organic condensate are listed in Table 1. Other typical properties of FPBO produced in the bioliq plant can be found in the work of Niebel et al.[19]

Table 1. Properties of the FPBO Used

properties	
water content	12 wt %
pH	3.7
density	1200 kg m^{-3}
solid content	6.4 wt %

2.2. Viscosity Determination and Sample Preparation. The viscosity was determined using a rheometer (Anton Paar, Modular Compact rheometer MCR 102). In this context, the viscosity of a liquid is measured in an autoclave in order to facilitate measurements at elevated pressure and at a defined temperature.

The measurements are performed with a helix spindle (see Figure 1). Unlike systems with a cylinder or cone-and-plate geometry, there is no defined laminar flow with a helix spindle and the definition of a gap for this geometry is not applicable. Consequently, the measurement of absolute viscosity is not possible. However, this geometry has the advantage to carry out robust measurements with high-viscosity FPBOs, which possibly show significant inhomogeneity, even when appearing homogeneous.

Each measurement is prepared by loading the measuring cell with the liquid to be tested according to the manufacturer's specifications and by conducting the measurement at a shear rate of 100 s^{-1} with a rotating spiral. At shear rates >60 s^{-1}, Newtonian behavior can be approximately assumed at the applied temperatures. One measuring point, as shown in Figure 3, refers to at least four measurements. Multiple measurements for pure FPBO ($n \geq 5$) shown in Figure 3a,c indicate an error interval of 1−2% for the procedure described by one standard deviation.

The gaseous CO_2 is taken directly from the liquid gas cylinder, which is why measurements are conducted with gaseous CO_2 up to a pressure of 50 bar. The gas is introduced into the top of the autoclave, forming a CO_2 layer on top of the liquid mixture.

FPBO in the condition received from the pyrolysis plant and blends of FPBO with 5, 10, and 15 wt % of ethanol are used as liquids. For CO_2 pressure-dependent measurements, the FPBO is exposed to gaseous CO_2 at a constant pressure. Ethanol (99.95%, CAS RN 64-

Figure 1. Helix spindle.

17-5) was purchased from VWR Chemicals BDH and carbon dioxide (99.995%, CAS RN 124-38-9) from Air Liquide.

The temperature-dependent viscosity was measured at different temperatures between 25 and 100 °C progressing with a temperature ramp of 2 °C min^{-1}. All other measurements were conducted at 25 °C. In the case of measurements under pressure, the corresponding pressure was held for at least 600 s, which was found to be sufficient to attain equilibrium. For the evaluation, the viscosity at a test time of 300 s was used, to avoid possible scattering of the viscosity values at later test times.

The rheometer is controlled with the associated Anton Paar RheoCompass 1.20 software, which records not just viscosity data but also shear stress and temperature. The CO_2 pressure is manually set and noted. Its integrated manometer with a deviation of 2 bar serves as a pressure indicator.

2.3. Relative Viscosity and Model Parameter Estimation. All viscosity measurements give the relative viscosity η_{rel}. This is the ratio of the measured viscosity η to the viscosity $\eta_{298\ K}$ of pure FPBO at 25 °C (eq 1). The relative viscosity has the advantage that it is measured using a nonconical spindle such as a helix spindle, which has a lower flow resistance (see Figure 1). This procedure simplifies the measurement of liquids with a greater viscosity. However, the applied measurement method does not lead to absolute values and, therefore, requires a reference value. In our context, the viscosity of pure FPBO at 25 °C is used.

$$\eta_{rel} = \frac{\eta}{\eta_{298K}} \tag{1}$$

with

η measured viscosity
η_{298K} measured viscosity at 298.15 K.

The applied models represent the exponential Arrhenius-type approach, resembling the Arrhenius equation[35] and the Vogel–Fulcher–Tammann equation (VFT equation). In the case of an ordinary liquid, the viscosity decreases as temperature increases. For these liquids, the corresponding activation energy E_{visc} is given with a positive sign. It can be regarded as a measure for the energy required for the liquid to flow.[29,31,38−40] The corresponding equations are represented by eqs 2 and 3. Combining these equations with eq 1 leads to the logarithmized eqs 4 and 5. They are the corresponding expressions with the relative viscosity.

$$\eta = A_A \times \exp\left(\frac{\Delta E_{visc}}{R \times T}\right) \tag{2}$$

with

η viscosity in mPa s
A_A pre-exponential factor in mPa s
ΔE_{visc} formal flow activation energy in J mol^{-1}
R universal or molar gas constant in J mol^{-1} K^{-1}
T temperature in K

$$\eta = A_{VFT} \times \exp\left(\frac{B_{VFT}}{T + C_{VFT}}\right) \tag{3}$$

with

A_{VFT} pre-exponential factor in mPa s
B_{VFT}, C_{VFT} constant factors in K

$$\ln\left(\frac{\eta}{\eta_{298K}}\right) = -\frac{\Delta E_{visc}}{R \times 298.15K} + \frac{\Delta E_{visc}}{R} \times \frac{1}{T} \tag{4}$$

$$\ln\left(\frac{\eta}{\eta_{298K}}\right) = \frac{B_{VFT}}{298.15K - C_{VFT}} - \frac{B_{VFT}}{T - C_{VFT}} \tag{5}$$

Both model approaches are descriptions for the relation between the viscosity and the temperature T. For the Arrhenius-type approach, the two parameters (the Arrhenius factor A_A and the activation energy E_{visc}) are employed. As mentioned before, E_{visc} can be interpreted as an energy of activation for the viscous flow, as defined by transition state theory.[41] The VFT equation results in the empirical parameters A_{VFT}, B_{VFT}, and C_{VFT}. It is often used because it is more suitable for a better fit to experimental data than an Arrhenius-type approach.[42] Therefore, the VFT equation is used for comparison.

3. RESULTS AND DISCUSSION

3.1. Temperature Dependency of FPBO and FPBO Blend Viscosity. To determine the temperature dependence, FPBO is heated to temperatures of 25−100 °C, as the viscosity is measured. At higher temperatures, an increasing tendency toward aging reactions can be expected and has previously been observed.[43] The relative viscosity obtained is plotted over the temperature in Figure 2a. This shows that the viscosity decreases with the temperature, which is similar to what can be expected and to what is known from other liquids[44] and FPBOs.[29−31,43] In Figure 2b and c, the data have been transformed into the Arrhenius plot and the plot related to the VFT equation (VFT plot), respectively. The plot parameters for all measurements are listed in Table 2. Both graphical representations clearly show that scattering occurs at temperatures above 61 °C. At higher temperatures, the torque drops below 0.2 mN m in two of the three measurements, which may be a limitation of the testing method. Therefore, this temperature is marked by a dotted line in Figure 2a−c and only viscosity values below 61 °C are considered for the fit.

For the pure FPBO in its supplied state, the average formal activation energy derived from the Arrhenius plot equates to 66.2 kJ mol^{-1}. For calculation purposes, the three measurements are averaged by determining the line of regression based on the slope and y-intercept. The error of the slope and y-intercept has the same magnitude as the measurements and lies at 1%. By Gaussian error propagation, this leads to a relative error interval of 1%. The received activation energy of the FPBO measured here indicates a high-viscosity liquid. Glycerol, for example, has a relatively high formal activation energy of 60 kJ mol^{-1} as compared to ethylene glycol (30 kJ mol^{-1}) and water (16 kJ mol^{-1}).[45] There was virtually no
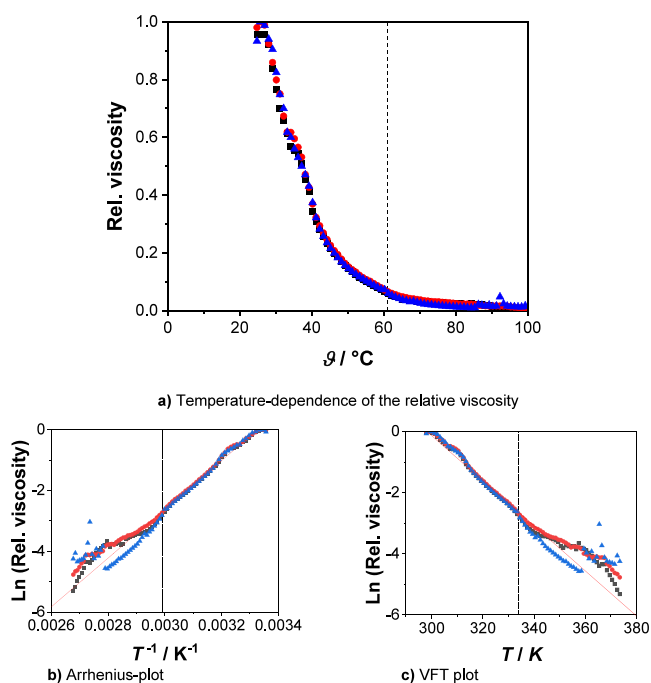
Figure 2. Plots of the viscosity measurements of pure FPBO conducted in triplicate, leading to three measuring curves indicated with different colors.

Table 2. Parameters Resulting from the Arrhenius Plot and the VFT Plot

Arrhenius			
liquid	E_{visc} (y-axis intercept)/ (kJ mol^{-1})	E_{visc} (slope)/ (kJ mol^{-1})	R^2
FPBO	66.2	66.8	0.990
10 bar/FPBO	41.9	42.0	0.983
5 wt % ethanol + 95 wt % FPBO	69.2	70.2	0.987
Vogel−Fulcher−Tammann			
liquid	B_{VFT}/K	C_{VFT}/K	R^2
FPBO	-1.05×10^9	1.19×10^5	0.983
10 bar/FPBO	-5.36×10^3	593	0.999
5 wt % ethanol +95 wt % FPBO	-3.95×10^7	2.81×10^4	0.980

21 kJ mol^{-1} for FPBO produced at similar temperatures from Norway spruce and white pine biomass. They conducted measurements at a shear rate of 200 s^{-1}.[31] The temperature range of measurements in both cases is similar to the measurement temperature range reported here.[29,31]

The fit achieved with the VFT equation shows a regression quality of $R^2 = 0.983$. Thus, it is somewhat below the goodness of fit achieved with the Arrhenius equation. Therefore, in viscosity measurements, the fit achieved with the VFT equation is not superior to the Arrhenius equation as Oginni and Tingi[31] have already demonstrated. The parameter C_{VFT} can be correlated with the glass temperature in the case of any glass being used. However, there is no practical application of this parameter for FPBO, since it is already a liquid mixture. The value of the parameter C_{VFT} is in the order of 10^5 K for the fit, as listed in Table 2.

The same procedure was also applied to FPBO blends with ethanol and CO_2. The first blend resulted from FPBO exposed to CO_2 at 10 bar, and a second blend was composed of 95 wt % FPBO with 5 wt % ethanol. The plot for the blend with CO_2 exhibits a linear behavior for temperatures up to 60 °C, and the mixture with ethanol is linear up to approximately 88 °C. Besides, they are very similar to the exemplary plots in Figure 2. The resulting plot parameters are also listed in Table 2.

A third blend combined the conditions of the first two blends. It consisted of 95 wt % FPBO with 5 wt % ethanol and was exposed to CO_2 at 10 bar. This resulted in a viscosity too low to be measured under the conditions of the previous measurements. It is less than 10% of the original viscosity of pure FPBO.

The formal activation energy E_{visc} for the blend with ethanol is similar to that of pure FPBO, leading to a value of 70 kJ mol^{-1}. It is somewhat greater but close to that of pure FPBO. This means that ethanol has hardly any effect on E_{visc} of FPBO. In contrast, the addition of CO_2 to FPBO reduces E_{visc} by nearly 40%.

As alluded before, scattering for FPBO with CO_2 occurred at 60 °C. This can be deduced to a limitation of the method by the torque or changes of the FPBO. In the FPBO−CO_2 system, a lower formal activation energy was measured. This is possibly related to the CO_2 desorption from FPBO because less CO_2 is dissolved in FPBO at higher temperatures, which is similar to other liquids, causing the blend to appear less viscous.

Similarly, Radovanovic et al. observed that gases desorb from FPBO above a certain temperature, making it difficult to determine the viscosity in their work. They suggested that desorbed gases are formed when FPBO starts to decompose at a certain temperature. This implicates that these gases were not solved before. They distinguished between two temperature ranges: a range below the decomposition temperature and a range above the decomposition temperature. Below the decomposition temperature, viscosity measurements could be conducted reliably; above the decomposition temperature, the values for the viscosity fluctuated. The obtained decomposition temperatures for several FPBOs made of pine were between 20 and 75 °C. The analysis of the desorbed gases revealed a composition of water, alcohols, organic acids, and esters, possibly resulting from aging and decomposition reactions.[43]

Their observations also match this work. The measurement range may be divided into two distinct temperature ranges separated by a decomposition temperature. At temperatures above this level, the formation and desorption of gases can take
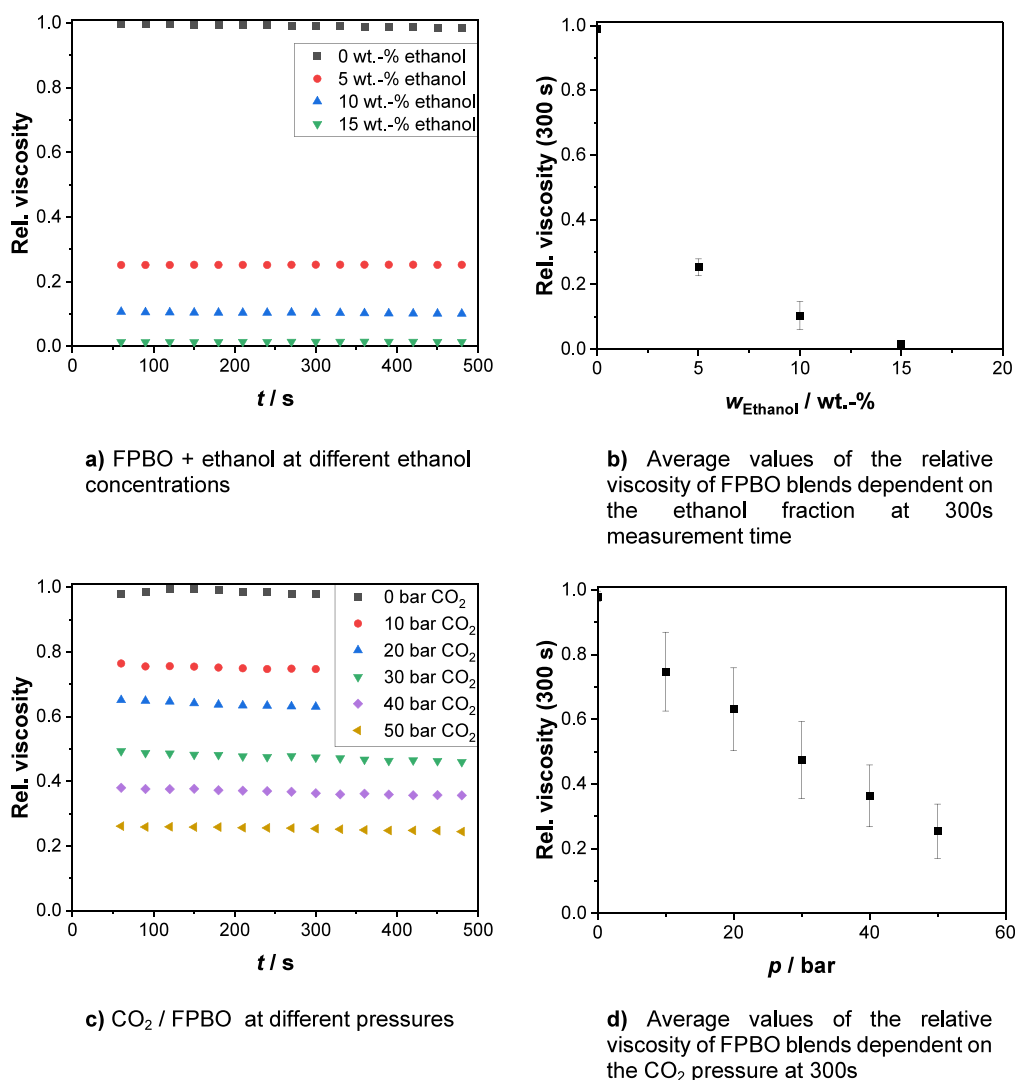
difference between the formal activation energies calculated based on the slope or y-intercept. The difference between the results of these two methods of derivation was also in the range of 1%. Consequently, for the evaluation of the remaining measurements, the slope is utilized, showing a goodness of fit of $R^2 = 0.990$.

Nolte and Liberatore[29] also determined the formal activation energy E_{visc} of FPBO by means of an Arrhenius approach. Their measurements resulted in 67 kJ mol^{-1} for FPBO produced from oak wood and 66 kJ mol^{-1} for FPBO based on poplar wood. Both FPBOs originated from a pyrolysis process performed at 500 °C. For another oak-derived FPBO produced at 600 °C, the activation energy was found to be significantly lower, at 24 kJ mol^{-1}. Their viscosity measurements were conducted at temperatures up to 55 °C.[29]

The formal activation energy of our straw-based FPBO shows a value similar to that of the oak and poplar FPBOs used by Nolte and Liberatore, which were produced at comparable temperatures. Their measurements were conducted at a shear rate of 100 s^{-1}.[29] Oginni and Tingi reported values of 16 and

Figure 3. Reduction of the relative viscosity of FPBO by dilution with ethanol and CO_2 at 25 °C.

place. Besides a limitation imposed by the torque limit in viscosity measurements, this could be another measurement limitation.

With respect to the goodness of fit, the VFT equation and the Arrhenius-type equation are comparable. Both have an $R^2 \geq 0.98$. On the one hand, the VFT equation is somewhat more suitable for the blend with CO_2. On the other hand, the R^2 value obtained with the VFT equation for the other measurements with pure FPBO and FPBO with ethanol is smaller. Thus, the VFT equation does not generally show a significantly better goodness of fit when applied. Furthermore, its variables provide hardly any useful physicochemical information. Therefore, the Arrhenius-type equation can be selected.

3.2. Concentration Dependency of the Viscosity of FPBO with Ethanol and CO_2 as a Solvent. In addition to the temperature-dependent behavior of the viscosity of FPBO and its blends, the concentration-dependent behavior of ethanol and CO_2 added to FPBO is examined in this section. For this purpose, measurements were carried out at a constant temperature of 25 °C. To determine the influence of ethanol, measurements were conducted with FPBO using three ethanol blends with different ethanol concentrations. The impact of CO_2 on the viscosity of FPBO was determined at different

CO_2 pressures. The pressure was increased in steps of 10 bar to 50 bar in the process. Each measurement was repeated at least three times.

The results obtained are shown in Figure 3. In the left column, the relative viscosity is plotted against the measurement time for FPBO with ethanol and CO_2 at different concentrations and pressures, respectively. It can be seen that the viscosity is hardly time-dependent during the measurement interval, indicating no pronounced rheopectic or thixotropic behavior. In the right column, the mean values for the relative viscosity are plotted against the ethanol concentration and the CO_2 pressure, respectively. The deployed relative viscosity belongs to a measurement time of 300 s. The error interval is derived from the standard deviation of the three individual measurements. For the ethanol measurement, the error interval is in the range of 0.2−52%, increasing with the ethanol quantity. For the CO_2 measurement, it equates to 2−33%, increasing with the CO_2 pressure. Generally, the viscosity of FPBO decreases exponentially with the ethanol concentration and linearly with the CO_2 pressure, as can be seen in Figure 3. In both cases, however, the viscosity is reduced by the quantity of the solvent. An ethanol concentration of 5 wt % decreases the original viscosity by 70−80%, as does a CO_2 layer of 50 bar

pressure. This means that no harsh conditions are necessary to induce this effect.

3.3. Implications of CO_2 as an Additive. Regarding the utilization of FPBO, some parameters such as the viscosity, the solid content, and water content are detrimental.[8,27] Therefore, the implications of the viscosity are discussed in this section. A high viscosity impedes further processing steps, such as filtration or pumping. The viscosity can be reduced by warming FPBO or adding solvents. The solid content unfavorably influences the combustion behavior of FPBO, but it can be reduced by filtration in advance. The water content can also limit the burning behavior, including the heating value. However, the water content of FPBO improves the flow properties required for further processing.[27]

However, other common solvents improve the flow properties similarly to water.[32] Consequently, this is why alcohols are often recommended as additives.[7,8] In principle, they can alleviate problems arising due to a high viscosity and the aging effect.[34] CO_2 can be a viable alternative to alcohols as it is a noncondensable gas, which is produced as a byproduct during the pyrolysis process. CO_2 does not reduce the corrosiveness or increase the calorific value, but, like ethanol, CO_2 can reduce the viscosity and, possibly, related properties such as density and surface tension. Consequently, the utilization of CO_2 can reduce aging during storage and facilitate processing steps such as pumping, filtration, and atomization in a burner.

The energy required for pumping liquids must be taken into account in technical processes. In oil refineries, approximately 40% of the electrical energy required is used for pumping purposes.[46] Accordingly, the pumping process significantly contributes to the operational costs of the process[47] and its environmental performance. In the context of crude oil, the energy required for liquid transfer through pipelines by pumping primarily depends on the pressure drop and, thus, on the viscosity as a consequence of flow resistance.[47,48] It is very likely that these factors also affect the processing and utilization of FPBO in technical plants.

Moreover, processing steps can be conducted more easily if the oil has a low viscosity. To reduce the viscosity, the standards ASTM D7544-12[8] and EN 16900:2017[7] recommend the addition of additives, especially alcohols, besides preheating FPBO before its usage as a burner fuel. However, preheating FPBO to improve pumping also requires energy and using additives is an additional cost factor.[32,49] Moreover, our measurements and the work of Radovanovic et al.[43] indicate that aging reactions already take place at moderate temperatures, possibly starting from approximately 60 °C within the context of this work. Therefore, the strategy of preheating has limitations.

Instead of preheating, additives may be more favorable. Besides, additives can also reduce the clogging of lines. Although alcohols (which are available on a renewable basis) are usually used for this purpose, this work shows that CO_2 has similar effects and leads to results comparable to those achieved with dissolved ethanol with regard to the viscosity. Because CO_2 is produced as a byproduct during the pyrolysis process, CO_2 may be an alternative to other additives. With CO_2, a significant viscosity reduction of FPBO by around 1 order of magnitude can be achieved if a pressure of 50 bar is provided. Once again, a similar process for crude oil already exists. In order to extract crude oil more effectively, the

viscosity is adjusted with short-chain hydrocarbons, flue gas, or carbon dioxide, among others (enhanced oil recovery).[50]

Atomization and fuel injection into a combustion or gasification chamber may also profit from a lower viscosity and higher pressure,[49] which can be generated by the same means as before. These conditions favor the rapid mixing of fuel and air, which is more important in smaller combustion chambers. Other factors determining the droplet size distribution during atomization are the surface tension and density of the burner fuel.[49] In addition, the expansion of the decompressing gas may contribute to an additional atomization energy during injection.

Also, a low viscosity can facilitate the separation of solids from FPBO after production, which is limited by the viscosity of the FPBO.[51] The separation of the solids formed during fast pyrolysis by hot-gas cyclones and filtration is an established process, which can improve the quality of FPBO as early as during the production process.[27,51−53] The separation of solids downstream of the production process is useful only if FPBO has a sufficiently low viscosity. The surface tension is another determining variable for the effectiveness of filtration.[54] The effectiveness of filtration can be defined by the filtrate flow minus added solvents (net filtrate flow), as long as the separation is not reduced.[54]

To assess the applicability for the filtration of FPBO under CO_2, the work from Sarrade et al.[55] can be used as orientation, because it enhances the understanding of the filtration process for multicomponent mixtures with polymeric components. They filtered used motor oil and related model blends containing poly(ethylene glycol) under pressurized CO_2. The experiments with model blends showed an increase of the net filtrate flow by a factor of 1.5−2 after decreasing the viscosity by a factor of 4−10. The viscosity was adjusted via the temperature and the CO_2 pressure. As shown and discussed above, an increase in both factors lowered the viscosity. The overall viscosity decreased with a declining average molar mass of poly(ethylene glycol). In subsequent experiments with the used oils, it was found that the filtration of oils with low viscosity was not improved but the filtration of oils with medium and high viscosity was. The improvement of filtration had the same order of magnitude as the reduction in viscosity.[55] From that, they concluded that apart from the viscosity, interactions with the applied filter material might play a role, because the pores of the filter could become clogged and, thus, reduce the filtrate flow.[55,56] As their work demonstrates, the filtration of FPBO with added CO_2 could be performed analogously. However, the choice of the filter material probably still plays a decisive role.

4. CONCLUSIONS

The viscosity of FPBO can be reduced by an increase in temperature as well as by the addition of ethanol and CO_2, with each strategy having advantages and disadvantages. An increase in temperature is a reliable method recommended by the standards ASTM D7544-12[8] and EN 16900:2017.[7] However, heating FPBO is an energy-consuming process that promotes aging reactions. Another recommended method is the deployment of additives, specifically alcohols. Besides the viscosity, they can also reduce the acidity of FPBO. On the other hand, CO_2 is a byproduct of the pyrolysis process and thus may be used as an added solvent. Pressurized CO_2 at 50 bar reduces the original viscosity of the wheat-straw-based FPBO used here by 70−80%, as does 5 wt % ethanol in FPBO.

Further measurements have shown that a comparable viscosity reduction is achieved by the same mass fraction of solved CO_2.[57] Since the molar mass of CO_2 and ethanol is quite similar, this implies a similar mole fraction. Higher amounts of ethanol induce a higher viscosity reduction, reaching less than 90% of the original viscosity with an ethanol fraction of 15 wt %. Generally, viscosity reduction can be useful to improve process steps such as storage, pumping, atomization, and filtration, which could also be achieved by adding of CO_2 from pyrolysis gas.

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Notes

The authors declare no competing financial interest.

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