Mixing of Fast Pyrolysis Oil and Black Liquor: Preparing an Improved Gasification Feedstock

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ABSTRACT: Co-gasification of fast pyrolysis oil and black liquor can be used to increase the size and improve profitability of pulp mill integrated biorefineries. The acids present in pyrolysis oil limit the amount that can be mixed into black liquor without causing precipitation of the black liquor dissolved lignin. This work shows that a simple model based on pyrolysis oil total acid number, including weak phenolic acids, can be used to predict the maximum pyrolysis oil fraction in blends. The maximum oil fraction is 20–25% for typical pyrolysis oil but can be increased up to at least 50% mass, corresponding to 70% energy, by addition of base. Thermodynamic equilibrium calculations are used to understand the effects of blend composition, including any added base, on the performance of a commercial scale gasification process. A substantial increase in overall gasification efficiency is observed with increasing pyrolysis oil fraction.

INTRODUCTION

Fast pyrolysis oil (FPO) is an interesting intermediate for production of transportation fuels and chemicals from various types of biomass. The liquid form and higher energy density can facilitate logistics and transport,1,2 but depending partly on the biomass type used, it is not certain that costs are always decreased.4 A number of upgrading pathways for FPO to transportation fuels and chemicals can be envisaged.5–8 FPO upgrading using entrained flow gasification as a first step is facilitated by the liquid form of the oil which allows feeding to a pressurized process and atomization of the feed.5,7

Gasification of black liquor (BL), a byproduct from the pulp and paper industry, is a promising technology for production of renewable fuels and chemicals9,10 that has been attempted with a range of technology variations.11,12 A 3 MWth pilot plant for pressurized oxygen-blown entrained-flow BL gasification (BLG), located in Piteå, Sweden, has accumulated >25 000 operating hours of which >8000 h with syngas upgrading to biofuel.10 The pilot plant has been used in a number of research studies to increase the understanding of various aspects of the technology.13–17

The catalytic activity of alkali metal salts in the black liquor is known to be important for the high reactivity of black liquor18–21 that enables production of a clean syngas at relatively low temperatures in an entrained flow gasifier.15 It has been shown in laboratory experiments that the alkali salt concentration in synthetic BL can be decreased approximately a factor ten without significantly decreasing the reactivity,18 which indicates that catalytic activity is maintained at much lower alkali concentrations than occur in industrial black liquors. Pilot scale experiments with a spent pulping liquor having an alkali content that is approximately 50% of that in BL seem to confirm this.22,23

It has recently been proposed that cogasification of pyrolysis oil and black liquor can be used to increase the size and flexibility of BLG based biorefineries and to improve profitability.24,25 Entrained flow gasification of FPO (without BL mixing) has been demonstrated but shown to require higher temperatures in order to obtain high carbon conversion and low levels of syngas impurities26,27 but still with lower carbon conversion in pilot scale than reported for BLG.17 However, if FPO is mixed with BL, the reactivity of the mixture has been shown to be the same as for pure BL,21 which indicates that similar reaction conditions can be used as for BLG to obtain similar process performance. Results from pilot scale gasification experiments with up to 20% FPO in BL confirm this.28–30

To use the catalytic activity from alkali, the material to be gasified must be in good contact with the alkali. Hence, feeding the BL and FPO streams separately to a gasifier will not give the same effect as supplying them as a mixture, since the contact between BL alkali and FPO droplets will in that case be poor. It has been noted that for blends of typical BL and wood based FPO, a lignin precipitate is formed at higher FPO fractions than approximately 25%,21 which could cause practical problems with feeding in a commercial implementation of the technology. At higher FPO mixing fractions, the acidity of FPO causes the pH of the mixture to be lower. This causes lignin precipitation because Kraft lignin solubility is lower at pH below 11.27,28 Hence, FPO acid number (AN) is an important parameter for the FPO/BL mixing process discussed in this paper. The pH, which is typically 2–3 for FPO30 and in general not directly correlated to AN,30 is important, for example, for material selection but not for FPO/BL mixing, since it is mainly determined by the strongest acids in FPO and not the total acid concentration.30

Positive effects on gasification process efficiency from FPO addition in BL gasification feedstock can be expected due to the decreased inorganic ballast and improved production economies of scale,34,35 but these studies did not consider the practical miscibility of FPO and BL. Hence, to determine the...
potential of this new technology it is of great interest to
investigate what determines the maximum fraction of FPO that
can be mixed into BL and still give a manageable gasification
feedstock with sufficient reactivity. Hence, the primary
objective of this work is to quantitatively understand the
maximum FPO fraction that can be mixed into BL for varying
FPO and BL properties and, in particular, to predict how FPO
acidity influences the amount of FPO that can be mixed into
BL without causing lignin precipitation. We also investigate if
addition of a base can increase this fraction. Another objective
is to assess cold gas efficiency (CGE) and oxygen consumption
for the feasible FPO/BL mixtures through process simulation
and in particular quantify any negative effects from any added
base on these parameters.

**EXPERIMENTAL SECTION**

**BL Sample.** The BL used in the mixing experiments was taken
from the LTU Green Fuels gasification pilot plant in Piteå, Sweden
and originated from the adjacent Smurfit Kappa Kraftliner Piteå pulp
mill. BL was analyzed for water content (SCAN-N 22:96), heating
value (bomb calorimetry) and element composition at SP Technical
Research Institute of Sweden (elemental analyzer for C, H, N;
ion chromatography on combustion products for S and Cl).
Remaining alkali in BL was determined by acid titration (SCAN-N
33:94) at MoRe Research, Örnsköldsvik, Sweden. LHV and sulfur free
LHV (SF-LHV) were calculated from HHV and composition. SF-LHV
is calculated from LHV by assuming that sulfur in the sample is not
oxidized during combustion, that is, ends up as sodium sulfide. The
motivation for using this heating value is that a commercial BLG
implementation requires all BL sulfur to be returned to the pulp mill in
reduced form and, hence, sulfur oxidization energy cannot be
utilized.17 Composition and properties of the BL are shown in
Table 1.

Table 1. Black Liquor Composition and Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BL sample for mixing experiments</th>
<th>typical BL used for simulations</th>
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</thead>
<tbody>
<tr>
<td>Water content (%)</td>
<td>24.4</td>
<td>25.0</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>52.5</td>
<td></td>
</tr>
<tr>
<td>C (%)</td>
<td>30.7</td>
<td>33.86</td>
</tr>
<tr>
<td>H (%)</td>
<td>3.7</td>
<td>3.45</td>
</tr>
<tr>
<td>O (%)</td>
<td>35.9</td>
<td>36.21</td>
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<tr>
<td>S (%)</td>
<td>5.7</td>
<td>5.03</td>
</tr>
<tr>
<td>Na (%)</td>
<td>20.6</td>
<td>18.97</td>
</tr>
<tr>
<td>K (%)</td>
<td>3.1</td>
<td>2.29</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Cl (%)</td>
<td>0.19</td>
<td>0.11</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>HHV (MJ/kg dry)</td>
<td>12.90</td>
<td>13.37</td>
</tr>
<tr>
<td>LHV (MJ/kg dry)</td>
<td>8.55</td>
<td>8.85</td>
</tr>
<tr>
<td>SF-LHV (MJ/kg dry)</td>
<td>7.18</td>
<td>7.66</td>
</tr>
<tr>
<td>Residual alkali (g NaOH/kg dry)</td>
<td>34.7</td>
<td>34.7</td>
</tr>
</tbody>
</table>

*As received, that is, including water. By difference. “SF-LHV” is sulfur free heating value, see text.*

**FPO Samples.** Five different FPO samples were used, all produced
from stem wood feedstock. The sample denoted VTT was produced
from the process development unit located at VTT Technical
Research Centre of Finland (Espoo, Finland)11 using pine sawdust
as feedstock. The pyrolysis temperature was 480 °C and oil recovery
was done with two scrubbers at 40 and 35 °C. The sample denoted
BTG was produced in the pilot scale rotating cone reactor located at
BTG Biomass Technology Group (Enschede, Netherlands)33 from
dried pine stem wood. Pyrolysis temperature was approximately 510 °C with
hot vapor residence time less than 2 s. Oil was collected from a spray
column condenser at 40 °C. The FPO sample denoted Fortum was
produced in the Fortum pyrolysis demonstration plant (Joensuu,
Finland)33 using wood chips as feedstock. The two FPO samples
denoted ETC-C and ETC-A were produced in a ablative cyclone at SP
Energy Technology Center (Piteå, Sweden). The formed pyrolysis oil
was collected in two separate steps: condensation using a water cooled
heat exchanger, giving the condensed fraction (ETC-C), followed by a
rotating disk stack where the aerosol coalesced into droplets, giving the
aerosol fraction (ETC-A). The used samples came from runs in which
the heat exchanger was improved giving a lower temperature, 7 °C130
instead of normally 25 °C,131 see Wiinikka et al.132 and Johansson et
al.134 for detailed description of process setup and oil properties.

FPO samples were analyzed for water content, element composition
and acid number at VTT. Element composition and water content
were determined using an elemental analyzer and a modified Karl
Fischer titration, respectively. Acid number determination included
both a carboxylic acid number (CAN) determination according to
a modified ASTM D664 procedure and a total acid number (TAN)
determination using isopropyl alcohol as solvent and tetra-n-butyl
ammonium hydroxide as titrant for improved sensitivity. The latter
method enables detection of weak acids e.g. phenolic hydroxyl
groups.135,136 Higher heating value of FPO was determined by bomb
calorimetry (KCA C200) at LTU. FPO composition and properties are
presented in Table 2.

In addition, two samples with higher acid content were prepared by
mixing the BTG FPO sample with acetic acid (denoted BTG-Ac1 and
BTG-Ac2). For BTG-Ac1, 4.32 g of anhydrous acetic acid was mixed
into 47.699 g of BTG FPO. For BTG-Ac2, 8.628 g of anhydrous acetic
acid was mixed into 42.776 g of BTG FPO. The amount of acetic acid
was determined with the aim of increasing total acids in the sample by
33% and 67% respectively, see Table 2.

**BL-FPO Mixing.** Preliminary mixing experiments carried out with
concentrated black liquors at 90 °C showed that it was very difficult to
achieve good mixing because of the high viscosity. The viscosity of 160
75% dry solids black liquor is >1000 mPa s at even 90 °C.181
In addition, neither filtering nor pH measurement of the final BL/FPO
mixtures is feasible for the warm concentrated mixtures, which in
combination with the very strong color of the mixtures means that the
detection of any precipitate was not feasible without dilution of the
mixtures. Hence, dilution of the mixtures by addition of water to a final
mixing dry solids (DS) content of 30% had to be used to make the
mixing experiments feasible and repeatable. Possible effects of this
dilution are discussed in the Results and Discussion section.

Initial experiments, aiming at determining at which pH that lignin
precipitation occurred in the mixtures, were executed using VTT and
BTG FPO according to a procedure very similar to the one described
below for quantitative mixing experiments. The results showed that a
pH of at least 10.9–11.0 is required to avoid precipitation that can be
detected by filtration in agreement with BL lignin precipitation
studies.17,28

For all FPO samples the maximum fraction that can be mixed into
BL without causing problematic precipitation was determined by the
following procedure. Approximately 30 g of BL was weighed in a 179
plastic container (Nalgene 250 mL LDPE) with optional addition of
70% NaOH as described further in the Results and Discussion section.
Water corresponding to 150% of the predicted total mass of BL,179
NaOH and FPO was added and BL was dissolved under mixing. FPO183
was loaded in a syringe and subsequently slowly added to the BL184
container under intense mixing (CAT mixer, T17N shaft). FPO was
added in small amounts followed by pH measurement using a glass
electrode adapted for dirty and sulfur containing samples (Mettler
Toledo DGI 114-SC) to varying pH in the interval 10.7–11.1, that is,185
slightly wider than the critical pH of 10.9 identified in initial
experiments. At this point, 50 mL of the mixture was filtered through a 190
cm diameter P2 glass filter (40–100 μm pore size) attached to a 191
suction flask. The appearance of the filter and the maximum pressure
drop over the filter were noted. Filtrations resulting in a pressure drop
193
Table 2. FPO Composition and Properties

<table>
<thead>
<tr>
<th></th>
<th>VTT</th>
<th>BTG</th>
<th>Fortum</th>
<th>ETC-C</th>
<th>ETC-A</th>
<th>BTG-Ac1</th>
<th>BTG-Ac2</th>
<th>typical^d</th>
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<tbody>
<tr>
<td>water</td>
<td>26.8</td>
<td>26.5</td>
<td>28.9</td>
<td>29.3</td>
<td>3.0</td>
<td>24.3</td>
<td>22.1</td>
<td>25.0</td>
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<tr>
<td>C (% dry)</td>
<td>55.2</td>
<td>55.4</td>
<td>55.7</td>
<td>56</td>
<td>5.6</td>
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<tr>
<td>H (% dry)</td>
<td>6.7</td>
<td>6.6</td>
<td>6.5</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>N (% dry)</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
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<td>HHV (MJ/kg dry)</td>
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<td>23.3</td>
<td>23.6</td>
<td>22.8</td>
<td></td>
<td>15.7</td>
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</tr>
<tr>
<td>LHV (MJ/kg a.r.)</td>
<td>15.6</td>
<td>15.5</td>
<td>15.5</td>
<td></td>
<td>15.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAN (mg KOH/g a.r.)</td>
<td>65</td>
<td>71</td>
<td>62</td>
<td>75</td>
<td>55</td>
<td>130^e</td>
<td>188^f</td>
<td>175</td>
</tr>
<tr>
<td>TAN (mg KOH/g a.r.)</td>
<td>174</td>
<td>176</td>
<td>144</td>
<td>127</td>
<td>146</td>
<td>235^g</td>
<td>293^h</td>
<td></td>
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</table>

^As received, that is, including water. ^eCalculated based on BTG sample and acetic acid addition. ^fTypical FPO used for simulations, see text.

RESULTS AND DISCUSSION

BL/FPO Mixing Experiments. To develop an understanding and quantifiable model of maximum FPO fraction in FPO/BL mixtures, FPO samples with varying AN are required to span a relevant experimental domain. Despite the fact that the five FPO samples were of different origin, using three different pyrolysis technologies, namely fluidized bed (VTT, Fortum), rotating cone (BTG) and ablative cyclone (ETC-A), the CAN and TAN numbers were fairly consistent at 55–75 and 127–176 mg KOH/g FPO respectively. A partial explanation is that all FPO samples were manufactured from stem wood feedstock. To create a wider TAN range, acetic acid was added to two FPO samples as shown in Table 2.

Figure 1 shows maximum tolerable FPO fraction in FPO/BL mixtures for FPO samples with varying TAN. The close agreement between experiments for the same oil samples shows that repeatability is acceptable. It is clear that the maximum FPO fraction is dependent on FPO TAN in a close to linear fashion, except for the ETC-A sample. This sample is different since it is collected from an aerosol and has very low water content compared to other samples (Table 2) and to what is typical for FPO. Further, it has very high viscosity, which may lead to poorer mixing resulting in locally lower pH values creating lignin precipitation.

The maximum tolerable FPO fraction as a function of CAN acids, shown in Figure 2, does not yield the same correlation that is obtained for TAN (Figure 1); the dependence seems to be opposite for samples with and without acetic acid addition. For samples without acid addition, Figure 2 actually shows a trend indicating that the maximum FPO fraction is higher for...
higher FPO CAN, which clearly does not agree with the observation that lower mixture pH causes lignin precipitation. These observations indicate that CAN is not as relevant as TAN for predicting maximum FPO fraction in FPO/BL mixtures.

This result can be explained in light of the acids detected by the CAN and TAN methods, respectively. The CAN method excludes weak acids ($pK_A > 9$). Low molecular weight carboxylic acids, primarily acetic, formic and glycolic acid, typically constitute approximately 4–7% of FPO but are still responsible for 60–70% of CAN. Other groups of compounds contributing to FPO CAN are hydroxy acids, sugar acids, extractives and lignin fragments but the $pK_A$ of lignin-related phenols and extractives have a wide range from 7 to 11, meaning that acidic groups in lignin fragments and extractives in FPO are only partially included in CAN.

The modified TAN method can be used to detect also weak acids in FPO samples including acids with a $pK_A$ up to approximately 11, which can give a better estimate of the total acids in FPO that is more relevant for FPO/BL mixtures. The large difference between CAN and TAN in Table 2 clearly illustrates the abundance of weak acids in the FPO samples. If enough alkali to precisely neutralize all acids included in TAN is added to the FPO, the resulting mixture will have a pH of approximately 11. As noted above, a pH $\geq 11$ gives a mixture without lignin precipitation. Hence, a simple theoretical model was developed that calculates the amount of FPO that can be added to a BL sample so that the added total FPO acids equal the BL residual alkali, theoretically giving a mixture with pH of approximately 11. This will give an indication of the maximum FPO addition that does not give lignin precipitation. This simple theoretical model, based on equal molar amounts of BL residual alkali and FPO acids, is shown as lines in Figure 1 and Figure 2. It is clear that the Fortum and ETC samples are closer to the theoretical line than the BTG and VTT samples, which was also evident from Figure 1. The reason for this is not completely understood but the different properties of the FPO samples are believed to be.

It can be concluded that the maximum FPO fraction does increase with the amount of added NaOH. Further, the simple theoretical model captures the trend even if, as also observed from Figure 1, the actual maximum FPO fraction is higher than predicted by the model.

Figure 4 combines data from Figure 1 and Figure 3 by plotting total mixture acids (FPO TAN) as a function of total alkali (BL residual alkali + added NaOH). It is clear that the Fortum and ETC samples are closer to the theoretical line than the BTG and VTT samples, which was also evident from Figure 1. The reason for this is not completely understood but the different properties of the FPO samples are believed to be.

Figure 2. Maximum FPO fraction m/m in FPO/BL mixtures for FPO samples plotted as a function of FPO CAN. The samples are the same as in Figure 1. The dashed line represents equal amounts of FPO acids and BL residual alkali.

Figure 3. Maximum FPO fraction, FPO/(FPO + BL) m/m, in FPO/BL mixtures for VTT and BTG FPO samples with varying amounts of NaOH added. The dashed line represents equal amounts of FPO acids and BL residual alkali, including added NaOH.

Figure 4. FPO acids (FPO TAN) as a function of total alkali (BL residual alkali + added NaOH) for all mixtures at maximum FPO fraction. The dashed line indicates equal amounts of acids and bases.
important. The Fortum sample is the only one produced in a commercial scale plant, but with a technology that is similar to the VTT pilot plant (fluidized bed). For the VTT and BTG samples adding base to BL or acetic acid to BTG FPO does not seem to change the “excess FPO acids”, that is, the vertical distance to the theoretical line in Figure 4. This indicates that the different behavior of FPO samples is not a consequence of varying FPO fraction in the final mixtures but rather due to other properties for the specific FPO samples. The ETC-A sample is the most extreme sample in Figure 4, which may be explained by the very low water content and higher viscosity leading to lower apparent lignin solubility.

In general, the results show that the amount of FPO that can be mixed into BL is higher than what is predicted by the simple theoretical model. There are a number of possible explanations for this. First, it is possible that the measured acid and base concentrations (FPO TAN and BL residual alkali) are not accurate or relevant for this application. The standard for BL residual alkali (SCAN-N 33:94) acknowledges and corrects for other strong bases than hydroxide but the amounts of these are not large enough to explain the difference between the experimental results and the theoretical model. Second, and more probably, it is possible that alkali to deprotonate all FPO weak acids is not required to keep phenolic lignin fragments in solution or suspension. The presence of any fragments in suspension that passes through the filter has not been measured in our experiments. Such suspended compounds are not likely to lead to practical problems in a gasifier feeding system.

Considering the general agreement between model and data and the fact that the model reproduces trends from both increasing FPO TAN and increasing BL alkali (through base addition), it is concluded that the simple model can be useful for predicting maximum FPO fraction in BL/FPO for cogasification applications.

When the results are to be used practically, it is important to consider the effect of the dilution of BL that was necessary in the mixing experiments (see Experimental Section), which can have some effect on mixture properties and component solubilities. The dilution decreases ionic strength, which has been shown to increase lignin solubility at constant pH and temperature. The amount of lignin precipitated from BL by acidification with carbon dioxide has been shown to depend on BL DS in the 10–50% range for precipitation of 40–70% of the total BL lignin. The latter result may not be completely relevant for the present study due to the high amounts of precipitated lignin. In the present work, it is the onset of precipitation that is aimed at predicting. As shown by the results discussed above, the major influence on lignin solubility comes from the balance between BL alkali and FPO acids giving the final pH of the solution. This balance is not influenced significantly by water addition. Thus, lab experiments with a lower DS concentration than would be used in a commercial application of the cogasification technology can be relevant also for applications with high DS content. It can also be noted that the use of the theoretical model gives conservative predictions (Figures 1 and 3), that is, that the predicted maximum tolerable FPO fraction is lower than the experimentally determined, the only exception being the ETC-A sample with very low water content.

### Feasible BL/FPO Mixtures with up to 50% FPO

The theoretical model based on BL residual alkali, including any added NaOH, and FPO TAN, discussed above, was used with typical BL and FPO compositions according to Table 1 and Table 2 to calculate the amount of NaOH required to avoid lignin precipitation for mixtures with up to 50% FPO (mass/mass). A 75% NaOH solution was assumed to be used as NaOH addition, since this is the same water content as the BL and FPO and thus removes any effects of different water content in the mixtures and also makes all compositions given valid on both dry and wet basis. Results are shown in Figure 5.

As noted above, these results are conservative, since the experimental results show that a higher fraction of FPO can be used without precipitation problems. However, since a practical implementation of the technology will always require a margin, the results are considered a realistic estimate of what could be achieved in a commercial implementation of cogasification technology.

According to Figure 5, no NaOH is needed for mixtures with up to 20% FPO. From 25% FPO the amount of NaOH gradually increases with increasing FPO fraction and is 5.7% at 50% FPO. The added NaOH influences the properties of the mixtures, for example, Na/C ratio and heating value as shown in Figure 6. From Figure 6a, it can be concluded that Na/C ratio decreases with increasing FPO fraction because of the low alkali content of FPO but that the addition of NaOH makes the decrease smaller than what would otherwise have been the case. It is very important to note that Na/C is higher than the approximate critical limit for catalytic activity extracted from the work of Verril et al. and also higher than Na/C than the pilot scale experiments previously reported for a low sodium spent pulping liquor from a sulfite cellulose mill. This result in combination with laboratory scale cogasification experiments with up to 30% FPO and pilot scale cogasification experiments with up to 20% FPO confirm that the Na concentrations in the mixtures according to Figure 5 are enough to maintain catalytic activity. It can be noted that the added NaOH is not required to maintain catalytic activity since also the dashed line of Figure 6a is above the critical limit for all mixtures. Hence, the NaOH addition required to avoid lignin precipitation is probably a disadvantage for the gasification process, since it is not likely to increase reactivity but adds thermal ballast and decreases heating value as shown in Figure 6b.

### Gasification Performance

On the basis of the expected similar reactivity of all mixtures, thermodynamic equilibrium simulations with some empirical modifications, as described above, were made for all mixtures in Figure 5 assuming the same global reactor temperature. Gasifier oxygen requirement is...
The slope change, most easily seen in the oxygen-to-fuel lower for mixture with higher FPO fractions as shown in Figure thermal ballast as noted above. The results in Figure 7 are addition required to avoid lignin precipitation, which adds FPO when going above 20% FPO is caused by the NaOH CGE decrease. Figure 7b, indicate a very high FPO-to-syngas conversion BL gasification experiment previously reported, green, dash) and the approximate limit for maintained catalytic activity according to Verril et al., red, dash-dot shown for comparison. (b) Mixture HHV (blue, solid) and LHV (green, dash-dot). Hypothetical values without NaOH addition are also shown (blue dash and green dot).

Figure 6. (a) Na/C (mol/mol) for the feasible mixtures of BL/FPO/NaOH (solid blue line) and the Na/C ratio that would have resulted without NaOH addition (long dash blue line). Na/C in the sulfite thick liquor gasification was 65% and 77%. It can be noted that SF-LHV CGE increases from 73% to 80% with increasing FPO fraction. The corresponding numbers for LHV CGE are 65% and 77%.

By comparing CGE of cogasification with gasification of pure BL it is possible to calculate the incremental CGE of added FPO. The incremental CGE of added FPO is defined as the increment in energy output (in syngas) divided by incremental energy input in FPO assuming the same efficiency of BL gasification with and without FPO. It thus represents the efficiency with which FPO can be converted to syngas using a BL gasification baseline. The results, shown as dashed lines in Figure 7b, indicate a very high FPO-to-syngas conversion efficiency in the range 82−86% depending on mixture and CGE definition used. A decrease in incremental CGE for added FPO when going above 20% FPO is caused by the NaOH addition required to avoid lignin precipitation, which adds thermal ballast as noted above. The results in Figure 7 are similar to what has been published before in a techno-economic assessment of FPO/BL cogasification but the previous study did not include the effect of NaOH addition at FPO levels above 20%. Figure 7 shows that the effect of NaOH addition required to obtain a homogeneous feedstock is relatively small, corresponding to a decrease in FPO incremental CGE by 1−2%−units (by comparing incremental FPO CGE at 10%, 30%, and 50%). It can, however, be noted that the efficiency of the total process increases monotonously with increasing FPO fraction, which means that higher FPO fractions are still preferable from a total process efficiency point-of-view.

To assess if cogasification with BL is a preferred process for conversion of FPO to syngas it is necessary to compare with what efficiency can be obtained by entrained flow gasification of (unblended) FPO. Simulations of FPO gasification were executed using the same thermodynamic model and the same assumptions as for FPO/BL mixtures but with a lower feed preheat temperature (50 °C) because of the coking tendency of FPO upon heating. The results show that a global gasification temperature of less than 1000 °C have to be used to obtain CGEs of 85% or more. Carbon conversion and methane formation cannot be estimated using the equilibrium model. It is, however, very likely that entrained flow gasification of FPO at such low temperatures could not be accomplished without significantly lower carbon conversion and higher methane formation. A gasification temperature range of 1250−1450 °C is more likely for a commercial process based on published pilot scale experiments for FPO and FPO/char slurry, leading to a lower CGE for gasification of pure FPO than the 82−86% incremental CGE observed for added FPO in the FPO/BL.
Cogasification process. Hence, the cogasification process seems to offer better conversion efficiency for FPO also when the addition of extra alkali is required at high FPO fractions. It can be noted that, recently, the potential role of alkali metals in pyrolysis oil conversion has also received attention with promising results regarding tar reduction. A large scale process utilizing this effect, however, probably still requires a lot of R&D effort.

In BLG and the cogasification technology BL inorganics are recovered in an aqueous solution called green liquor (GL), mainly in the form of carbonate, Na₂CO₃, and sulfide, Na₂S. In the chemical preparations section of the pulp mill, the carbonate is transformed to the active pulping chemical NaOH by reaction with calcium oxide, which is called caustizing. Any NaOH added to the BL/FPO mixture to keep lignin in solution will end up in the GL together with the Na content in the BL and can be transformed to NaOH together with the rest of the carbonate in the GL stream, which enables reuse of the added NaOH but leads to some costs for the extra capacity required in the caustizing process.

The calculations presented in Figure 6 were made using a typical BL residual alkali, as noted above, but in practice residual alkali is not constant. Figure 8 shows the distribution of residual alkali in the BL from the Smurfit Kappa Kraftliner Piteå mill, which is the source for the BL used in the experiments. The value used in the calculations, 34.7 g of NaOH/kg BL corresponding to 46.3 g of NaOH/kg BL solids, matches the mean of the distribution (50.1 g NaOH/kg BL solids) well but if the 10th and 90th percentiles of the distribution are considered the amount of FPO that can be mixed without NaOH addition varies by ±21% (relative). An unexpected decrease in BL residual alkali would potentially create operational problems in a cogasification process by leading to lignin precipitation and thus a feedstock slurry that is difficult to handle. In addition, the gasifier simulation results indicate clearly the benefits of not adding more NaOH than required to keep the FPO/BL mixture homogeneous. Hence, control and monitoring of BL residual alkali will be important in a pulp mill that supplies BL to a cogasification process. If practically feasible, an approach including a pH measurement of the mixture could be very useful to improve gasification efficiencies by not adding more NaOH than necessary while still keeping the pH high enough to avoid lignin precipitation.

**CONCLUSIONS**

The maximum fraction of FPO that can be blended into BL without addition of other components is dependent on FPO TAN, including phenolics, and the amount of residual alkali from pulping present in the black liquor. For typical FPO and BL the maximum FPO fraction is 20–25% by mass, corresponding to 34–40% by energy. It has been shown that mixtures with more than 50% FPO by mass, corresponding to 67% by energy, can be produced by adding a small amount of NaOH to increase mixture pH and avoid lignin precipitation. A simple theoretical model can be used to approximately predict maximum FPO fraction and/or the amount of added NaOH required to obtain a homogeneous gasifier feedstock mixture. The difference between model and experiments indicate that a limited amount of protonated phenolic lignin fragments can be kept in solution or suspension.

The necessary addition of NaOH at FPO fractions over 20% has a small negative effect on gasification efficiency but nevertheless a substantial increase in overall gasification efficiency is observed with increasing FPO fraction. Very high incremental FPO CGE values of 82–86% can be obtained, which is probably very difficult to obtain by direct entrained flow gasification for FPO. This implies that cogasification based biorefineries can be an attractive choice for FPO upgrading to chemicals or transportation fuels. The primary reason for the high efficiency of the cogasification process is the decreasing inorganic ballast while maintaining the catalytic activity of the inorganic components. This possibility is caused by the fact that BL contains an "overload" of Na. The greatly increased biofuels production capacity of up to 200% obtained when considering the amount of black liquor available at a specific pulp mill by cogasification of FPO with BL is valid regardless of the addition of alkali.

Finally, it can be noted that the mixing experiments described in this study are executed at high mixing intensity in very small scale. In a commercial application of the cogasification technology, it will be important to design an efficient mixing process to avoid pH gradients that can lead to precipitation of lignin even if this is not expected from global equilibrium.

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**Notes**

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