Co-gasification of pyrolysis oil and black liquor: optimal feedstock mix for different raw material cost scenarios

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Abstract

Black liquor gasification (BLG) has been shown to be advantageous regarding efficiency and economic performance compared to a new recovery boiler investment for pulp mills in many cases. One alternative to increase the motor fuel production volumes and to improve the operational flexibility of the BLG plant is to add pyrolysis oil (PO) to the black liquor (BL) feed and co-gasify the blend. The catalytic activity of alkali metals in the BL enhance the gasification rates, leading to a higher syngas quality achieved at lower temperatures when gasifying the blend compared to unblended PO. The objective of this techno-economic study was to determine the optimal PO addition for different PO price scenarios using the Rottneros Vallvik mill with BL gasification based methanol production as case study. The results show that good economic performance can be obtained for PO prices significantly higher than projected future commercial scale production costs for PO from lignocellulosic raw materials. By adding PO so that a 50/50 blend of BL and PO is gasified, it is possible to increase methanol production by more than 250% compared to BL gasification, which leads to significant economies of scale. However, the higher feedstock cost for PO will counteract this effect and the optimal feedstock mix is dependent on the prices of the feedstocks. The optimal PO addition is, hence, different for different PO price scenarios. It is concluded the co-gasification of BL and PO is an attractive investment opportunity for most PO price scenarios. The technology can increase the methanol production volume and add extra revenues per produced unit compared to methanol produced via gasification of pure BL or PO.

KEYWORDS: Black liquor, Pyrolysis oil, Co-gasification, Methanol, Pulp mill

Introduction

Pyrolysis oil (PO) can be produced from various types of biomass such as straw, wood and wood waste, through a variety of technologies. There is a large interest in PO as a feedstock for production of green chemicals and fuels, where one viable route can be via gasification. Research has shown that a high gasification temperature or a catalytic bed is required to produce a syngas with high quality from PO [1, 2]. One possible route to obtain catalytic effects is to blend PO with black liquor (BL), because the alkali metals in BL are known to catalyze gasification reactions [3-6].

Andersson, et al. [7] has showed that co-gasification of BL and PO receives a good economic performance for PO prices significantly higher than projected future commercial scale production costs for PO from lignocellulosic raw materials. That study considered two blend ratios; 25% and 50% PO addition on the total wet feed of BL. By gasifying a 50/50 blend, it was possible to increase methanol production by more than 250% compared to BL gasification, which led to significant economies of scale. Increasing PO prices may counteract this effect and the optimal BL/PO blend ratio is, hence, different for different PO price scenarios.

The main aim of this study was to techno-economically investigate integrated methanol production at a Swedish pulp mill (the Rottneros Vallvik mill) via co-gasification of PO and BL. Six methanol production capacities were considered for blends with up to 50% PO addition. The main objective was to find the optimal PO addition to the available BL feed at different PO prices.

Case description and modelling

The Rottneros Vallvik mill, located in Sweden, was used as case study. A fifty-fifty PO/BL blend ratio was considered as the maximum allowed addition where the alkali content in a blend still can provide sufficient catalytic effects based on experience of pilot plant sulphite thick liquor gasification [8]. PO addition was therefore considered to be in the range of 10-50% (i.e. Case 10-50) of the available volume of BL on a wet basis (2049 ton/d or 180 MW[1]). Pilot plant experiments to verify assumed co-gasification efficiencies and temperatures are currently being prepared.

The alternative system configurations were methanol produced via two routes: *i)* Case 0, via gasification of the available BL, and *ii)* Case 100, via gasification of unblended PO in a non-integrated gasification plant, with a PO input corresponding to a fifty-fifty blend (i.e. 365 MW).

Gasification plant modelling

Simulations of the gasification process were made for a 0-100% PO blend using a thermodynamic model developed for gasification of BL. Simulations represent a realistic gasifier size and heat losses for a commercial implementation of BL/PO co-gasification. Pure PO gasification was simulated using other assumptions about reactor temperature and heat losses due to the absence of catalytic alkali content respectively a different reactor design. An estimate reactor temperature of 1300 C was used based on information about the Karlsruhe Institute of technology Bioliq plant published before plant start-up[2] [9, 10]. The Bioliq process uses a cooling screen reactor, which normally leads to higher heat losses than a ceramically lined reactor; a 2% heat loss was used as an estimate. The BL gasification model and the modelling assumptions are further described in [7, 11, 12].

The integrated and the stand-alone configurations were represented by a modeled using Mixed Integer Linear Programming (MILP) through the Java-based software tool reMIND [13]. The steam/power balance for the downstream units for all cases were scaled according to a reference black liquor gasification (BLG) plant that produces 100 MW methanol [14] adjusted to the operation of the gasifier for the different blends (i.e. 0-100%). The pulp mill's power and steam balance was represented by a black box approach. The primary modeling constraint for the integrated cases was to ensure that sufficient amount of steam was available for the pulp making, done by adjusting biomass supply to the bark boiler. An off-gas boiler was required to generate steam to satisfy the internal demand in Case 100. The boiler was fuelled with the purged off-

[1] Sulfur free lower heating value (SF-LHV) was used as basis for calculations since the sulfur in the BL is returned in reduced form to the mill (as sodium sulfide in green liquor).
[2] Note that the Bioliq process uses a slurry including char but the simulations in this work was based on gasification of the same PO composition (see [7]) that was used for mixing with BL, i.e. without char.

gases from the methanol synthesis loop. In the other cases, surplus off-gases were used as a supplement to the lime kiln fuel, i.e. to reduce/remove the import demand of lime kiln fuel. A further description regarding the scaling parameters, modeling approach and the how the mill was affected by an integrated BL/PO gasification plant, can be found in [7]. All cases consider an external oxygen supply, i.e. "bought over the fence".

Figure 1 shows a schematic view of the different gasification plant configurations including the methanol synthesis.

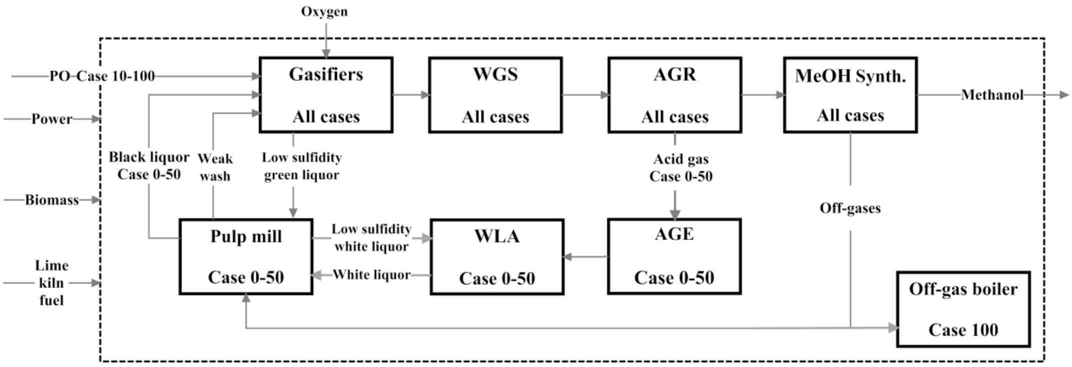

Figure 1. Simplified flowsheet for the different methanol production pathway.

Techno-economic evaluation

The plant operation was based to match a projected future yearly operation average of the Rottneros Vallvik mill during 348 days with 90% availability. This corresponds to a BL availability of 180 MW (SF-LHV) during 7517 hours [7]. The same overall capacity utilization was used for all cases. The co-gasification cases were compared to Case REF, which views the combination of Case 0 and Case 100 as one configuration. This was done to determine potential technical and economic added-values with co-gasification compared to the unblended gasification alternative.

The overall system efficiencies for all cases were calculated based on the marginal energy supply compared to the pulp mill with an upgraded recovery boiler including the utility requirements for the ASU[3]. PO was assumed to be delivered to the gate, but the effect a PO production efficiency in the range of 67-90% [15] has on the overall system efficiency was also included in the evaluation. Electrical equivalents were used as a measure of the overall system efficiency. The energy carriers (methanol, biomass, etc) were converted to their electricity equivalents according to the efficiency (η) of the best-available technologies known to the authors. The efficiencies are shown in **Table 1**. Biomass used directly for the pulp making was not included in the calculation of the overall energy system efficiencies. The system boundaries used is illustrated by the dashed boxes **Figure 1**.

Rottneros Vallvik mill has plans to increase the pulp production capacity. The single largest investment for increasing the capacity would be to upgrade/rebuild the recovery boiler. This would be avoided in all gasification cases. The incremental investment cost was therefore calculated for all system as a comparison between an investment in a rebuilt recovery boiler and methanol production via the gasification alternatives. The

[3] Note that oxygen was bought "over the fence" but the utility requirements for the ASU were included in the overall system efficiency calculations.

investment costs were scaled according to a reference based on a BLG plant producing 100 MW methanol [14].

Table 1. Power generation efficiencies used for calculation of electricity equivalents.

Energy carrier	Power generation efficiency (η)	Reference
Biomass	46.2%	[16]
Methanol	55.9%	[16]
LPG	57.6%	Assumed the same as for SNG [16]
Pyrolysis oil	50.0%	Assumed

The gasification unit uses a multi-train arrangement and the maximum capacity for each individual gasifier was based on what was commercially offered by Chemrec for BL gasification [14]. The thermal load capacity was assumed to be 20% higher when PO was added, due to the lower ballast in the reactor caused by decreased fuel ash content.

In **Table 2**, cost and selling price for the different commodities and products are listed. The methanol selling price was used for determining the internal rate of return (IRR) in a cash flow analysis[4], based on the PO price range. Note that the PO price range was not correlated to the biomass price in **Table 2**.

Table 2. Feedstock costs and product prices [14].

Consumables and products	Comment	Cost	Unit
Biomass	2.94 MWh/ton (40 % moisture)	28	€/MWh
Power		57	€/MWh
Oxygen		69	€/ton
Lime kiln fuel		46	€/MWh
Methanol		984[A]	€/ton

[A] Based on a volumetric equivalence to ethanol, which was considered relevant for low blend into gasoline.

Three different PO price levels were used to determine the optimal PO addition:
i) 45-60 €/MWh, a PO price range corresponding to rather favourable, but still reasonable, conditions (location, efficiency, biomass price, etc.) for PO production.
ii) 60-75 €/MWh, an intermediate price level where, for example, the biomass price and the transport cost represent a larger share in the price setting.
iii) 75-90 €/MWh, represent a scenario with prices that were significantly higher than projected future commercial scale production costs for PO.

Results and discussion

By co-gasifying a blend of biomass based PO with a fixed amount of BL the increased total feedstock flow and the higher heating value of the PO (4.27 MWh/ton at 25 % water content) can significantly increase the total energy input. As a result, the cold gas efficiency (due to lower ballast in the system) and the specific methanol output (per MW of input) were improved with increasing shares of PO added.

The co-gasification routes seem to be advantageous with respect to energy efficiency compared to methanol produced from a stand-alone PO gasification plant and via gasification of the available BL, (Case REF), see **Figure 2**. This was also valid when

[4] The analysis considers a three year construction time. During the first production year it was assumed that only 60% of the maximum methanol production capacity was achieved. Full production was not reached until the fourth year.

the losses in pyrolysing biomass to PO were accounted for. If PO can be produced with an efficiency around 90% the same system efficiency was received independent on the added amount of PO to the blend.

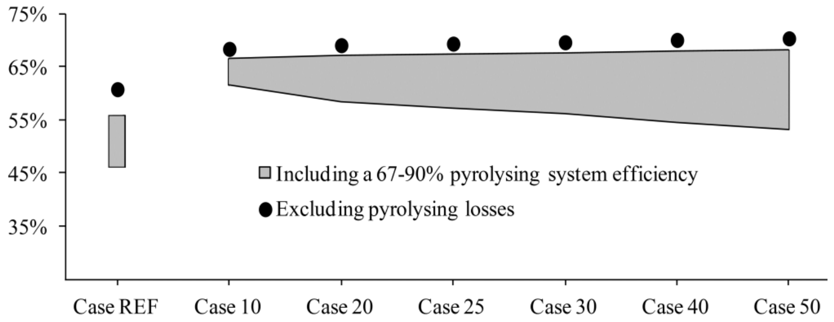

Figure 2. Overall system efficiency calculated using electricity equivalents.

The IRR on the investments in all cases are presented in **Figure 3** for the three PO price levels. Co-gasification was favourable compared to Case REF for all PO price levels. Based on the low and the intermediate price level (i.e. 45-75 €/MWh) the production profitability was improved with increasing PO content in the blend. The reason was mainly the favourable economies of scale effect obtained in the co-gasification routes that lower the specific investment cost. The exception in the trend was when the blend increases from 25% to 30%, which demanded one additional gasification reactor, i.e. a 5x20% design replaces 4x25%. The added investment for the extra reactor was not compensated by the higher methanol production capacity.

At the highest PO price level, the increased import cost for PO start to diminish the added-values from co-gasification the higher PO blends (Case 30-50). Case 20-25 would, for PO prices over 80 €/MWh, be the wisest solution considering received IRR, see **Figure 3**. This PO price level was, however, projected to be significantly higher than future commercial scale production costs for PO.

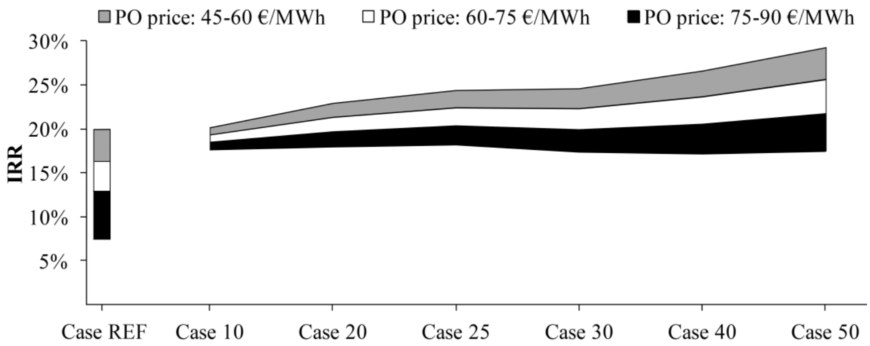

Figure 3. IRR for the different cases dependent on the PO price, methanol selling price 984 €/ton and no taxes considered.

As illustrated in **Figure 3,** Case REF could only be competitive with Case 10 for a PO price around 45 €/MWh. Even lower PO prices would be required if the methanol produced via stand-alone gasification of PO (Case 100) alone should be competitive with the co-gasification alternatives (not presented in **Figure 3**).

Conclusions

The main objective was to find the optimal blend of pyrolysis oil and black liquor for methanol production via integrated gasification. The results showed that co-gasification can improve the overall energy system efficiency and the economic benefits compared to methanol produced via black liquor gasification as well as via stand-alone gasification of pyrolysis oil. The main conclusion was that the production profitability was improved with the amount of added pyrolysis oil to the blend for pyrolysis oil prices up to 80 €/MWh. For higher pyrolysis oil prices a 20-25% pyrolysis oil addition would be more profitable.

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