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Co-gasification of pyrolysis oil and black liquor for methanol production

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HIGHLIGHTS

- Techno-economic results regarding biomass-based methanol production.
- Integration of a methanol production processes in a pulp and paper mill.
- Co-gasification of black liquor and pyrolysis oil for increased methanol production.
- High system efficiency for the methanol produced via co-gasification.
- Methanol produced via co-gasification is an attractive investment opportunity.

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ABSTRACT

One alternative to reduce the motor fuel production cost and improve the operational flexibility of a black liquor gasification (BLG) plant is to add pyrolysis oil to the black liquor feed and co-gasify the blend. The objective of this study was to investigate techno-economically the possibility to increase methanol production at a pulp mill via co-gasification of pyrolysis oil and black liquor. Gasifying a blend consisting of 50% pyrolysis oil and 50% black liquor on a wet mass basis increases the methanol production by more than 250%, compared to gasifying the available black liquor only. Co-gasification would add extra revenues per produced unit of methanol (IRR > 15%) compared to methanol from unblended BLG (IRR 13%) and be an attractive investment opportunity when the price for pyrolysis oil is less than 70 €/MW h. The economic evaluation was based on a first plant estimate with no investment credit for the recovery boiler and a methanol product value volumetric equivalent to conventional ethanol, both these conditions will not applicable when the technology has been fully commercialized.

1. Introduction

Production of renewable motor fuels and chemicals is important in the development toward a more sustainable society where fossil fuels are replaced. To be able to compete with fossil resources, efficient production of biomass based products is necessary to maximize overall process economics and to minimize negative environmental impact. In order to obtain reasonable production costs, large biorefinery plants will likely be required to yield favorable economy-of-scale effects [29]. Integrating large scale biofuel production processes in existing forest industries provides large feedstock handling and logistical advantages [1]. Gasification of black liquor can for example be applied in chemical pulp mills and has been successfully demonstrated in a 3 MW pilot plant in Piteå in Sweden [8,19,37]. Compared to combustion of black liquor in a recovery boiler, black liquor gasification combined with motor fuel production show advantages regarding economic performance and energy efficiency. The available volume of black liquor is however limited and strongly connected to the pulp production, which limits the potential motor fuel production. Furthermore a high availability of the gasification plant is required to ensure that crucial cooking chemicals in the black liquor are returned to the pulp mill. One way to increase the production of motor fuel as well as the operational flexibility of the black liquor gasifier is to add biomass based pyrolysis oil to the black liquor feed and co-gasify the blend.

Pyrolysis oil can be produced from various types of biomass such as straw, wood and wood waste, through a variety of technologies. Pyrolysis of biomass yields primary char, permanent gases, and condensable vapors [28]. The vapors can be recovered as viscous liquids via condensation. A fast pyrolysis (rapid heating) process results in a product that mainly consists of liquid bio-oils, i.e. pyrolysis oil [27,28]. Pyrolysis oil can be used in a number of applications, including co-firing with fossil fuels in power plants [5]. There is great interest in using pyrolysis technology for

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Nomenclature

Abbreviations

AGR	acid gas removal
ASU	air separation unit
BFP	biofuel plant
BLG	black liquor gasification/gasifier
CGE	cold gas efficiency
EFC	Elemental Chlorine Free bleached pulp
HP	high pressure
IRR	internal rate of return
LP	low pressure
MILP	Mixed Integer Linear Programming
MP	medium pressure
UKP	Unbleached Kraft pulp

production of green chemicals and fuels [10,11]. One possible route is to gasify pyrolysis oil to a syngas that can be used as raw material for various petrochemical processes [10,11,21].

Research has shown that a high gasification temperature or a catalytic bed is required to produce a syngas with high quality [33,34]. Without a catalytic material, gasification of pyrolysis oil requires substantially higher temperatures compared to gasification of black liquor to obtain a similar gas quality and carbon conversion. This is at least partly due to the lack of catalytically active alkali metals in pyrolysis oil. Alkali metals are known to catalyze gasification reactions [15,16,32] and this is believed to be an important explanation of the very high carbon conversion obtained for gasification of black liquor at relatively low global temperature of approximately 1000 C. By blending pyrolysis oil with black liquor it is possible to obtain catalytic effects in the co-gasification process [2]. The energy content in biomass based pyrolysis oil is almost twice as high as the black liquor energy content. A fifty-fifty blend (by mass) would therefore roughly triple the energy input to the gasification plant. This would result in increased production volumes and the economy-of-scale effects in the downstream gas conditioning and synthesis which may lower the production cost.

Catalysis of pyrolysis and gasification reactions from sodium salts is known to increase the reactivity of black liquor and black liquor char substantially [22,30,36]. Recent experimental work with pyrolysis oil and black liquor blends verifies the feasibility in the concept of co-gasification. It has been shown that mixtures containing up to 30 wt% pyrolysis oil and 70 wt% black liquor have a reactivity similar to pure black liquor [2]. This indicates that pyrolysis oil and black liquor blend can be co-gasified in a black liquor gasifier without major operational changes, e.g. using the same gasification temperature. Pilot scale pyrolysis oil/black liquor co-gasification experiments to validate and demonstrate the technology are underway in the 3 MW_{th} LTU Green Fuels pilot plant in Piteå, Sweden. A fifty-fifty blend of a typical pyrolysis oil and black liquor has many similarities to sulfite thick liquor, e.g. heating value and alkali metal content. During two experiments in the black liquor gasification pilot, sulfite thick liquor was gasified with excellent performance under virtually the same processing conditions normally used for the black liquor [13,14]. The sulfite thick liquor gasification experiments support that 50% less alkali content still provides sufficient catalytic activity to achieve the same very high carbon conversion and low tar content as for black liquor gasification without increased process temperature. This is further supported by the work of Verrill et al. [35] with, synthetic black liquors, where the same catalytic effects was obtained from sodium salts even if the sodium concentration was lowered to 10% of the normal concentration.

The main aim of this study was to investigate techno-economically the possibility to increase methanol production at a Swedish pulp mill (the Rottneros Vallvik plant) via co-gasification of pyrolysis oil and black liquor. The objective was to evaluate the feasibility of the incremental methanol production capacity compared to a black liquor gasification plant for methanol production. This was done by calculating the overall energy efficiency for two blend ratios, i.e. 25% and 50% pyrolysis oil of the total wet feed. The evaluation of the process economics was made with a cash flow analysis to determine the internal rate of return (IRR) for three different cases.

2. Material and methods

2.1. Gasification modeling

The gasification technology considered is the Chemrec pressurized oxygen-blown entrained flow black liquor gasification/gasifier (BLG) technology. The study of Bach Oller et al. [2] shows that the BLG process and co-gasification of black liquor and pyrolysis oil are very similar. They studied single droplet swelling, devolatilization rate and char gasification rate experimentally without finding any significant differences. This indicates that a similar catalytic effect from black liquor sodium content can be realized in the co-gasification process, although the alkali content of the mixed feedstock was lower. Hence, simulations of the co-gasification process were carried out using a thermodynamic model developed for BLG using the same process temperature (1000–1100 °C) but including the new mixed feedstock composition and heating value.

The thermodynamic simulation model uses thermodynamic data from Lindberg [23] for pure inorganic components and from Knacke et al. [18] for the remaining species. Based on flows of feedstock and required reactor temperature, the model calculates oxygen flow to the reactor and syngas composition. Empirical modifications, based on operating experience from the 3 MW_{th} BLG pilot plant in Piteå Sweden [8,26,37], were used for CH_4 and H_2S/COS concentrations in the gas, since these were not well described by thermodynamic equilibrium. The model has been validated against experimental data from the pilot plant and compared to CFD modelling of the process [7].

Simulations were made for a 0–50% pyrolysis oil blend and represent realistic sizes of an individual BLG in its commercialization phase, 70–85 MW_{th}, and heat losses for a commercial implementation of black liquor/pyrolysis oil co-gasification. Table 1 shows

Table 1
Black liquor and pyrolysis oil specification used for simulations.

	Black liquor [a] (%)	Pyrolysis oil [b]
Dry substance (DS) (wt%)	73.2%	75.0%
LHV MJ/kg dry	12.13	21.3
S (kg/kg dry)	5.52%	
Cl (kg/kg dry)	0.13%	
C (kg/kg dry)	32.50%	61.33%
H (kg/kg dry)	3.40%	4.30%
N (kg/kg dry)	0.08%	0.01%
Na (kg/kg dry)	20.23%	
K (kg/kg dry)	2.18%	
O (kg/kg dry)	35.96%	34.40%

[a] Model composition for pulp mill using the Kraft pulping process.
[b] From BTG Biomass Technology Group BV [6].