Greenhouse gas emissions of methanol from co-gasification of black liquor with by-product biomass

Olofsson, Johanna; Börjesson, Pål

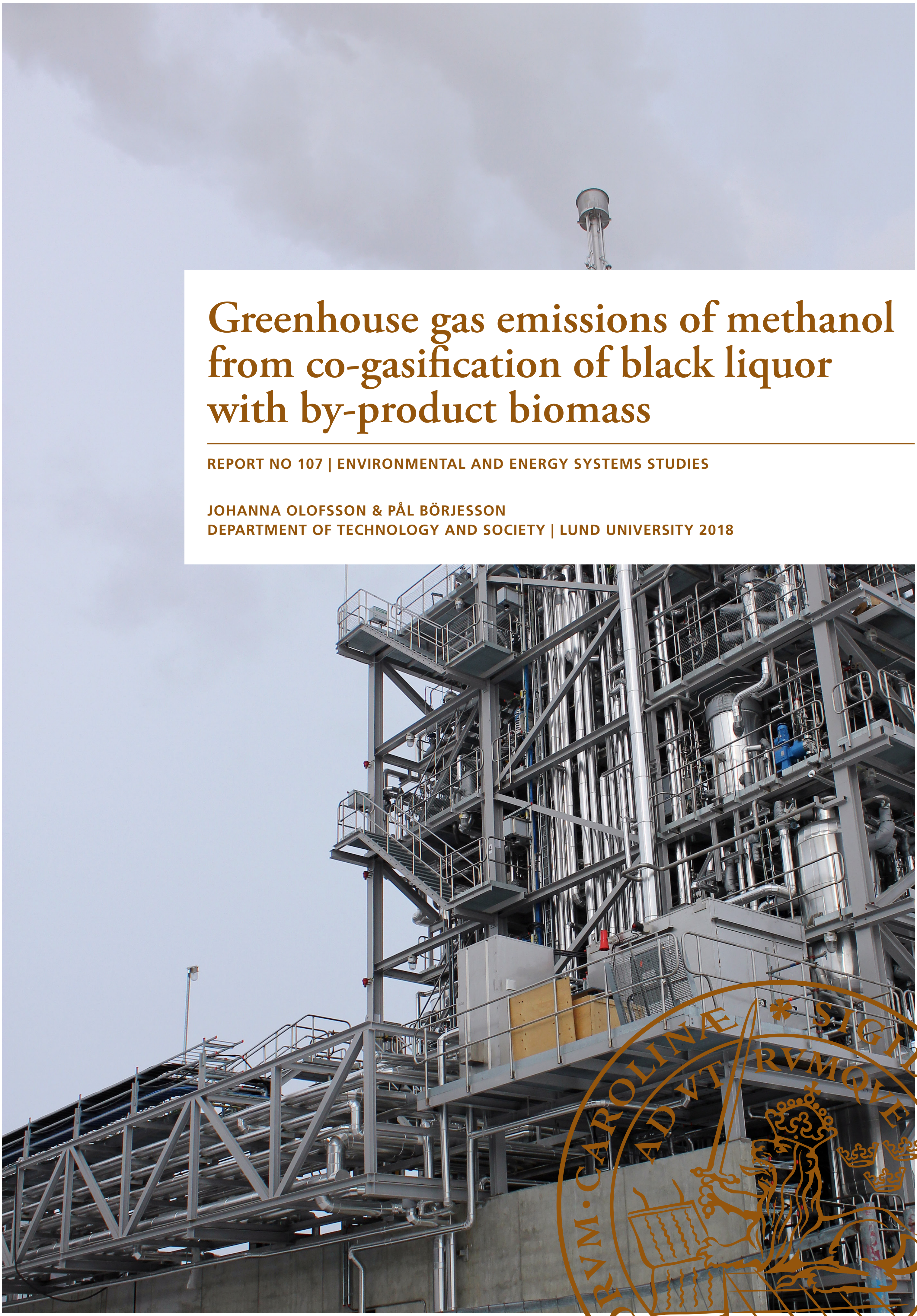
2018

Document Version:
Publisher's PDF, also known as Version of record

Link to publication

Citation for published version (APA):
Olofsson, J., & Börjesson, P. (2018). *Greenhouse gas emissions of methanol from co-gasification of black liquor with by-product biomass*. Miljö- och energisystem, LTH, Lunds universitet.

Total number of authors:
2



Greenhouse gas emissions of methanol from co-gasification of black liquor with by-product biomass

REPORT NO 107 | ENVIRONMENTAL AND ENERGY SYSTEMS STUDIES

JOHANNA OLOFSSON & PÅL BÖRJESSON
DEPARTMENT OF TECHNOLOGY AND SOCIETY | LUND UNIVERSITY 2018

Greenhouse gas emissions of methanol from black liquor co-gasification with by-product biomass

Johanna Olofsson & Pål Börjesson

LUNDS
UNIVERSITET

Report no. 107
Environmental and Energy Systems Studies
Department of Technology and Society

March 2018

Cover photo: Tomas Bergman

IMES/EESS Report No. 107

ISRN LUTFD2/TFEM-- 18/3098 --SE + (1-34)

ISSN 1102-3651

ISBN 978-91-86961-33-6

Preface

The present study was initiated within the project *Methanol production via black liquor gasification with expanded raw material base* (Metanolproduktion via svartlutsförgasning med utökad råvarubas) which was funded by the Swedish Energy Agency and f3 – Swedish Knowledge Centre for Renewable Transportation Fuels. In addition to the present report, a summary of the full project is available as:

> Lundgren, J., et. al., (2017) *Methanol production via black liquor gasification with extended raw material base*. Report No 2017:14, f3 The Swedish Knowledge Centre for Renewable Transportation Fuels, Sweden. Available at www.f3centre.se.

The authors of this report would also like to acknowledge additional funding from the Norwegian Research Council through the project *Sustainable path creation for innovative value chains for organic waste products* (SusValueWaste).

Summary

A sustainable transition of the transport system is likely to require different fuels, technologies and infrastructural changes, and among the many options are biofuels. A potential resource for biofuel production in Sweden, black liquor, a lignin-rich by-product from the pulp and paper industry, can be gasified and converted to methanol fuel. Though the amount of black liquor available is limited by pulp production, the potential for biofuel production could be extended by using other by-product biomass resources in co-gasification with black liquor, thus providing an extended resource base for gasification as well as providing a potentially efficient conversion process for by-products. As such, the benefits of a co-gasification scenario could be two-fold.

Among the potential by-product biomass resources that could be available for co-gasification with black liquor, this work considers three options:

i) pyrolysis liquid made from forest logging residues,
ii) crude glycerol from RME production,
iii) solid fermentation residues from lignocellulosic-ethanol production.

The potential to produce bio-methanol sustainably from the considered resources and co-gasification systems, however, also requires acceptable environmental impacts, among other aspects. The aim of this study is therefore to assess the greenhouse gas (GHG) emissions of fuels produced from co-gasification of black liquor with residual biomass, as well as the amount of fuel produced. In order to facilitate interpretation of the results, each co-gasification option is compared to a corresponding reference scenario with an assumed alternative handling of both the black liquor and the residual biomass (i-iii). For each residual biomass type, both a low-blend and a high-blend case is investigated, as well as two qualities of methanol transportation fuel.

The GHG emissions from co-gasification of black liquor with i) pyrolysis liquid, ii) glycerol and iii) fermentation residues were assessed using two complementary life-cycle based calculation approaches following the EU Renewable energy directive (RED) criteria and the ISO standards for life cycle assessment. For comparison to the co-gasification cases, the reference handling was assumed to be gasification of black liquor, direct gasification of logging residues, anaerobic digestion of crude glycerol, and combustion with power generation for fermentation residues.

The results differ between the different co-gasification cases, both regarding conclusions for GHG emissions and for fuel production. For logging residues, the extra conversion step of pyrolysis required for co-gasification entails losses that are not made-up for in co-gasification efficiency, and thus the reference scenario produces more methanol fuel. As for GHG emissions, the co-gasification and reference scenarios yield similar results, though the reference scenario shows slightly lower emissions for the high-blend case. For glycerol, similar amounts of transport fuel (methanol and methane) are produced in both scenarios, but with slightly lower GHG emissions in the co-gasification scenarios, mainly due to methane slip from anaerobic digestion processes. For fermentation residues, the low efficiency in producing electricity from combustion results in lower energetic output in the reference scenarios, and also with the difficulty in comparing electricity to methanol fuel. Concerning GHG emissions, no large differences between the co-gasification and reference scenarios can be noted, though the choice of RED or ISO methods for calculation affect the comparison. More specifically, the ISO method generally yields higher GHG emissions due to inclusion of additional processes. For all the studied cases, GHG emissions calculated according to the EU RED method show that all cases and scenarios fulfil the currently required 60 % GHG reduction target as compared to a fossil fuel reference.

The results are accompanied by various aspects of uncertainty, not least regarding by-product biomass availability and markets, and regarding future development of the Swedish energy system. Firstly, the

modelled co-gasification systems are based on the technical potential to blend by-product biomass into black liquor for co-gasification and methanol production in a future large-scale integrated pulp and biofuel plant, and the future availability of the biomass resources has not been explicitly considered in this report. Secondly, in each co-gasification system, electricity use contributes to a large share of the GHG emissions, and therefore the future electricity generation in the Nordic countries will affect the results. Other important parameters in terms of GHG emissions include the climate impact of removing logging residues which affects the soil carbon storage, as illustrated by ISO method calculations, and the alternative use of the by-product biomass resources.

The present study shows that co-gasification of black liquor with an extended raw material base is comparable to alternative technologies in terms of biomass to biofuel conversion efficiency and GHG emissions. As such, the investigated by-product biomass resources could increase the raw material available for methanol production through co-gasification, but co-gasification does not appear to provide a more efficient biomass to biofuel conversion of said biomass resources when compared to alternative handling options. Due to the mentioned uncertainties, however, the results should be interpreted with caution. More exhaustive analyses with specific data for each considered case would be needed in order to meet some of the uncertainties and to draw further conclusions.

Sammanfattning

En hållbar omställning av transportsystemet kan komma att kräva olika typer av bränslen, tekniker och infrastrukturförändringar, och som ett möjligt alternativ finns biodrivmedel. En potentiell resurs för biodrivmedelsproduktion i Sverige är svartlut, en ligninrik biprodukt från pappers- och massaindustrin, som kan förgasas och omvandlas till metanol. Mängden svartlut som finns tillgänglig begränsas av massaproduktionen men ett sätt att utöka potentialen för biodrivmedelsproduktion kan vara att blanda svartlut med andra typer av biomassabiprodukter i samförgasning, och på så sätt utöka råvarubasen för förgasning samtidigt som en potentiellt effektiv omvandlingsprocess för biprodukter till biodrivmedel görs möjlig. Därmed kan fördelarna med samförgasning vara dubbla.

Utav biomassabiprodukter som möjligen skulle kunna användas i samförgasning med svartlut utreds här tre alternativ:

i) pyrolysvätska gjord av grot,
ii) råglycerol från RME-produktion,
iii) fasta fermenteringsrester från cellulosabaserad etanolframställning.

Möjligheten att producera hållbart biodrivmedel från dessa resurser och samförgasningssystem kräver dock att ytterligare aspekter, däribland miljömässiga, beaktas. Syftet med denna studie är därför att utvärdera växthusgasutsläppen av bränslen från samförgasning av svartlut med biomassabiprodukter, såväl som mängden bränsle som dessa system kan producera. För att underlätta tolkning av resultaten jämförs dessutom varje samförgasningsscenario med ett referensscenario där alternativ hantering av både svartlut och biomassabiprodukt (i-iii) sker. För varje typ av biomassaprodukt utreds ett låginblandnings- och ett höginblandningsfall, samt produktion av två olika typer av metanolbränsle.

Växthusgasutsläppen från samförgasning av svartlut med i) pyrolysvätska, ii) råglycerol och iii) fermenteringsrester utreddes med två livscykelbaserade beräkningssätt, dels utifrån kriterierna i EU:s förnybarhetsdirektiv och dels utifrån ISO-standarderna för livscykelanalys. För referensscenarier antogs den alternativa hanteringen vara förgasning av svartlut, direktförgasning av grot, rötning (anaerobisk nedbrytning) av råglycerol och förbränning med elproduktion för fermenteringsrester.

Resultaten skiljer sig mellan de olika samförgasningssystemen både vad gäller växthusgasutsläpp och bränsleproduktion. För grot medför det adderade konverteringssteget i form av pyrolys, som är nödvändigt för samförgasning med svartlut, en förlust som inte kan kompenseras för av förgasningens omvandlingseffektivitet. Således produceras mer metanol i referensscenariot. Vad gäller växthusgasutsläpp ger samförgasnings- och referensscenarierna i liknande resultat, om än något lägre utsläpp för referensscenariot i höginblandningsfallen. För glycerol produceras liknande mängder drivmedel i samförgasnings- och referensscenarierna men med något lägre växthusgasutsläpp i samförgasningsscenarierna på grund av metanläckage från rötningsprocesserna. För fermenteringsrester resulterar den låga omvandlingseffektiviteten i elproduktionen till ett energimässigt lägre utbyte, men också med svårigheten att jämföra metanol och elektricitet. Växthusgasutsläppen är i grova drag jämförbara mellan samförgasnings- och referensscenarierna även om jämförelsen mellan systemen påverkas av valet av beräkningsmetod (RED eller ISO). Generellt ger ISO-metoden högre växthusgasutsläpp vilket förklaras av att fler processer inkluderas i beräkningarna. För samtliga studerade system visar beräkningar av växthusgasutsläpp enligt RED att alla fall och scenarier uppfyller det nuvarande kravet på 60 % utsläppsreduktion jämfört med en referens för fossilbaserat bränsle.

Med resultaten följer en rad osäkerhetsaspekter, inte minst vad gäller tillgänglighet till och marknader för biomassabiprodukter, och även vad gäller utvecklingen av det svenska energisystemet i stort. För det första baseras de modellerade systemen på den tekniska möjligheten att blanda biproduktbiomassa med svartlut för samförgasning och metanolproduktion i en framtida, storskalig, integrerad massa- och

biodrivmedelsanläggning. Framtida tillgänglighet till råvarorna har därmed inte beaktats explicit i denna rapport. För det andra bidrar elanvändning till en betydande del av växthusgasutsläppen för samtliga studerade samförgasningssystem och utvecklingen av det nordiska elsystemet påverkar på så vis resultaten. Andra viktiga parametrar att nämna i samband med osäkerhet och växthusgasutsläpp är klimatpåverkan från förändringar i skogsmarkens kollager till följd av grotuttag, som illustreras här med ISO-beräkningar, och den antagna alternativa användningen av biomassabiprodukter.

Denna studie visar att samförgasning av svartlut med en utökad råvarubas skulle kunna omvandla biomassa till biodrivmedel med en effektivitet och klimatprestanda som är jämförbar med alternativ hantering av biomassaresurserna. Därmed kan de undersökta biomassabiprodukterna utöka råvarubasen för metanolproduktion genom samförgasning med svartlut, men samförgasningen verkar inte ge några fördelar i termer av effektivitet och växthusgasutsläpp jämfört med andra möjliga tekniker som skulle kunna omvandla biprodukterna till biobränsle. På grund av nämnda osäkerhetsaspekter bör resultaten dock tolkas med försiktighet. Ytterligare utförliga studier med specifika data för varje enskilt fall skulle behövas för att adressera några av osäkerheterna och dra vidare slutsatser.

Contents

1. Introduction 1

2. Method 3

  2.1 System description and life-cycle inventory 4

    2.1.1 Black liquor, pulp mill and integrated biofuel plant 5

    2.1.2 Forest logging residues and pyrolysis 6

    2.1.3 Glycerol 7

    2.1.4 Fermentation residues 10

3. Results and discussion 12

  3.1 Black liquor and pyrolysis liquid 12

  3.2 Black liquor and glycerol 14

  3.3 Black liquor and fermentation residues 16

  3.4 Common observations and uncertainty 18

4. Conclusions 19

References 20

Appendix: Mass balances 22

  Co-gasification of black liquor and pyrolysis liquid 22

  Co-gasification of black liquor and glycerol 23

  Co-gasification of black liquor and fermentation residues 24

  Gasification of black liquor (reference case) 25

  Direct gasification of logging residues (reference case) 26

1. Introduction

A circular, biomass-based economy is today promoted as a means to mitigate negative anthropogenic environmental impact such as climate change. This proposed transition includes an increased utilization of biomass feedstocks, preferably by cascading, in combination with efficient and circular flows of resources and valorization of low or no-value residuals and waste products (Bugge et al., 2016; Murray et al., 2015; Keegan et al, 2013). A bioeconomy, where new products and economic value are developed from existing biomass waste streams by emerging technologies and integrated systems, will also require an increased collaboration between different industry sectors (Bugge et al., 2016). One example is new cooperation between the forest industry and the transportation fuel industry. A sustainable transition of the transport system is likely to require different fuels, technologies and infrastructural changes, and among the many options are biofuels. One potentially underutilized resource for biofuel production in Sweden is black liquor, a lignin-rich by-product from the pulp and paper industry which can be converted to bio-methanol through gasification. However, the amount of black liquor available is limited by pulp production, and thus the potential for fuel production through BL gasification is limited. One way to extend the potential for biofuel production through gasification could be to make use of other by-product biomass resources in co-gasification with black liquor, thus providing an extended resource base for gasification as well as providing a potentially efficient conversion process for by-products. The potential efficiency of the co-gasification alternative is due to the possibility for other biomass resources to benefit from the high reactivity of black liquor in the gasification process, which is mainly due to its high alkali content. The benefits of a co-gasification scenario could thus be two-fold.

Among the potential by-product biomass resources that could be available for co-gasification with black liquor, this work considers three options:

i) pyrolysis liquid made from forest logging residues,
ii) crude glycerol from RME production,
iii) solid fermentation residues from lignocellulosic-ethanol production.

Firstly, logging residues are a product of forest management and logging consisting of branches, tree tops and other material. Through a process of pyrolysis, logging residues can be converted to pyrolysis oil which is possible to blend with black liquor in co-gasification and methanol production (Bach Oller et al. 2015). Secondly, crude glycerol is a by-product from FAME (fatty acid methyl ester) biodiesel production. The type of FAME production affects the crude glycerol composition, but here we consider crude glycerol from RME, rapeseed-based biodiesel. Thirdly, solid and lignin-rich fermentation residues are a by-product of bioethanol production from lignocellulosic (woody) material. For fermentation residues and crude glycerol, both by-products from biofuel production, handling of the material is both necessary and beneficial in order to achieve viable production systems.

The technical potential of co-gasification of black liquor with other by-product biomass material is investigated in the project *Methanol production via black liquor gasification with expanded raw material base*. The potential to produce bio-methanol sustainably from the considered co-gasification systems, however, also requires acceptable environmental impacts, among other aspects. Within the area of biofuels, sustainability of production and use is most commonly governed through the GHG (greenhouse gas) emissions of different fuels from a life-cycle perspective. While widely used, the methodology of life cycle assessment (LCA) requires interpretation and choice from the practitioner which can lead to different and even contradictory results from different studies, not least for studies of productions systems which utilize residual biomass as feedstock (Olofsson et al. 2017). One way to handle these limitations is to apply different calculation methods in LCA's of residual-based biofuels to show how contrasting approaches affect the results. The aim of this study is to assess the GHG emissions of fuels produced from co-gasification of black liquor with residual biomass, as well as the amount of fuels produced per amount of feedstock. In order to facilitate interpretation of the results, each co-gasification option is compared to a corresponding reference scenario with an assumed alternative handling of both the black liquor and the residual biomass (i-iii). Thus the findings of this report adds to the overall assessment of the potential for black liquor co-gasification to provide biofuel to a future Swedish transportation system.

2. Method

The GHG emissions of methanol are assessed using a life cycle perspective and method which includes raw material production and processing in a so called well-to-tank analysis. The well-to-tank GHG emissions are quantified following the life-cycle based calculation approach as required by the EU Renewable energy directive (2009/28/EC), RED, rules for calculating GHG emissions from liquid biofuels (Annex V). The resulting life-cycle GHG emissions are combined with global warming factors as defined by the IPCC in order to estimate the impact on climate, and more specifically the global warming potential (GWP). The global warming factors used are 34 g CO_2-eq. per g CH_4 and 298 g CO_2-eq. per g N_2O (Myhre et al. 2013).

In addition to the EU RED method for calculating GHG emissions, parallel assessment is made according to the ISO standards for life cycle assessment, 14040 (ISO 2006a) and 14044 (ISO 2006b). A reason for using a second parallel calculation approach for life-cycle GHG emissions is the importance of method choices to life-cycle assessment results. Where RED calculations could be considered more relevant to current European policy requirements, ISO standards leave more room for interpretation and choice. In this study, the ISO calculations thus represent a type of sensitivity analysis to EU RED results, as they highlight some potential implications of changed calculation rules.

Comparing the two calculation approaches of RED and ISO, one important difference regards the inclusion of changes to soil organic carbon stock. According to the RED calculation rules, potential changes in soil organic carbon stock due to removal of logging residues are not included as long as the overall use of the land as forest land does not change. This is because only emissions "*from carbon stock changes caused by land-use change*" are to be included in calculations of GHG emissions from biofuels (RED Annex V), where land use change is defined by the Swedish Hållbarhetsförordning (SFS 2011:1088, §5) as a shift between two of six land use categories; forest land, grassland, agricultural land, wetland, built-up area and other land. Following ISO standards, however, no such rules are specified. Therefore the RED calculations in this study do not include soil organic carbon changes from removal of logging residues, while the ISO calculations do.

Another potentially important distinction in the RED calculation rules concerns by-products as resources, where the EU RED states that wastes and residues from processing should be considered to have no greenhouse gas emissions prior to their collection. The directive specifically mentions crude glycerol (glycerine) as one such processing residue:

> "Wastes, agricultural crop residues, including straw, bagasse, husks, cobs and nut shells, and residues from processing, including crude glycerine (glycerine that is not refined), shall be considered to have zero life-cycle greenhouse gas emissions up to the process of collection of those materials."
> (RED Annex V, point 18)

In their guidelines for the EU RED calculation method, the Swedish Energy Agency further mentions black liquor and crude glycerol as by-products to be considered to have zero life-cycle GHG emissions (Swedish Energy Agency 2012). Also logging residues are stated as zero-emission residues in the guidelines, but with requirements to fulfil the EU RED land criteria, e.g. regarding the type and status of forest land where residues are collected from (RED Article 17).

All calculations of GHG emissions from the studied systems, following the EU RED and the ISO standards guidelines, are based on data from the project *Methanol production via black liquor gasification with expanded raw material base*. In the project, lab and pilot scale experimental data was used as a base to model the co-gasification and methanol production (Carvalho et al. 2017a). The gasification simulations were carried out using the SIMGAS thermodynamic equilibrium model while the downstream syngas upgrading and bio-methanol synthesis was simulated in Aspen Plus. The following sections describe the studied systems and the inventory data used to calculate life-cycle GHG emissions.

2.1 System description and life-cycle inventory

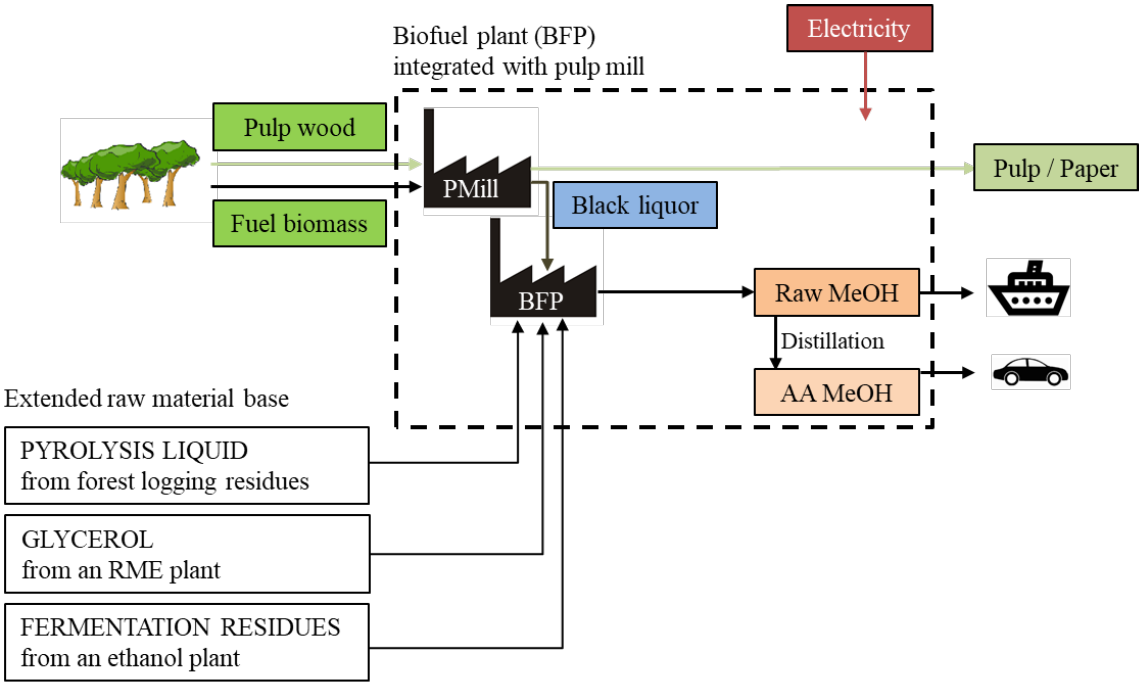


Figure 1. Schematic overview of integrated pulp mill (Pmill) and biofuel plant (BFP), producing methanol from black liquor and additional biomass. Fuel biomass is logging residues.

As basis for the co-gasification systems, this study considers a large pulp mill which produces 700 kADt (AD: air dry) of pulp per year through the sulphate or kraft process, which also generates black liquor as a by-product. The considered pulp mill is integrated with a biofuel plant which produces methanol through gasification of the black liquor – alone, or with additional biomass resources. Fig. 1 shows an overview of the general system setup. Regarding the by-product biomass resources considered in this study, three different systems are modelled and assessed: black liquor co-gasification with

iv) pyrolysis liquid from logging residues,
v) crude glycerol from RME production,
vi) solid fermentation residues from lignocellulosic-ethanol production.

For each of the considered co-gasification systems, a comparison is made to a reference scenario with alternative handling of the biomass resources. The alternative handling of black liquor is gasification in each system, and the alternative handling of by-product biomass types varies between the three studied systems:

i) direct gasification and methanol production for logging residues,
ii) anaerobic digestion and biogas production for glycerol,
iii) combustion with power production for fermentation residues.

Also for each co-gasification system, two mixing ratios for by-product biomass and black liquor are presented (based on Carvalho et al. 2017a). For pyrolysis liquid and crude glycerol, the assessment includes mixing rates of 20 % and 50 % by-product biomass by weight. For fermentation residues, mixing rates of 20 % and 35 % are investigated.

Adding to the assessment of each studied system, two qualities of methanol are studied as end-products: first, grade AA methanol which can be used as car fuel, and second, crude methanol which can be used as a maritime fuel and which does not require distillation, lowering production costs.

Table 1 summarizes the cases investigated for each of the three main co-gasification systems. In addition, each of the cases in table 1 is compared to a reference scenario with alternative handling of the biomass. The underlying modelling results for each co-gasification case i), ii) and iii), are available in appendix (table A 1 to A 3).

Table 1. Overview of the cases assessed for each co-gasification system.

By-product biomass	Mixing ratio (by-product biomass weight)	MeOH crude	MeOH AA
i) pyrolysis liquid (logging residues)	20 %	1.1a	1.1b
	50 %	1.2a	1.2b
ii) crude glycerol (from RME production)	20 %	2.1a	2.1b
	50 %	2.2a	2.2b
iii) fermentation residues (from ethanol production)	20 %	3.1a	3.1b
	35 %	3.2a	3.2b

2.1.1 Black liquor, pulp mill and integrated biofuel plant

The considered pulp mill takes in 107 tons of pulp wood and produces 82 tons of pulp per hour in all studied cases, which gives 4167 tons (80% dry matter, DM) of black liquor per hour as by-product (Fig. 1). For calculations of methanol GHG emissions, the pulp produced is not considered in the assessment. Also, the use of pulpwood is entirely allocated to pulp, and thus not included in the calculation of GHG emissions.

In all cases, electricity is considered to be a Nordic electricity mix with GHG emissions of 125.5 g CO_2-eq. kWh^{-1}, or 34.9 g CO_2-eq. MJ^{-1} (Martinsson et al. 2012).

In all reference cases, the alternative use of black liquor is direct gasification for methanol production (raw and grade AA), as illustrated in Fig. 2. The simulation results in terms of mass and energy balances for black liquor gasification are available in appendix (table A 4).

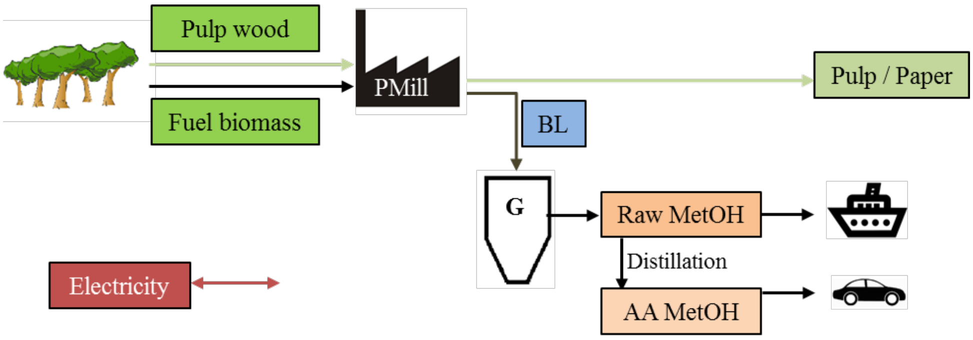


Figure 2. The considered alternative use of black liquor is direct gasification, which is applied in all studied reference cases.

2.1.2 Forest logging residues and pyrolysis

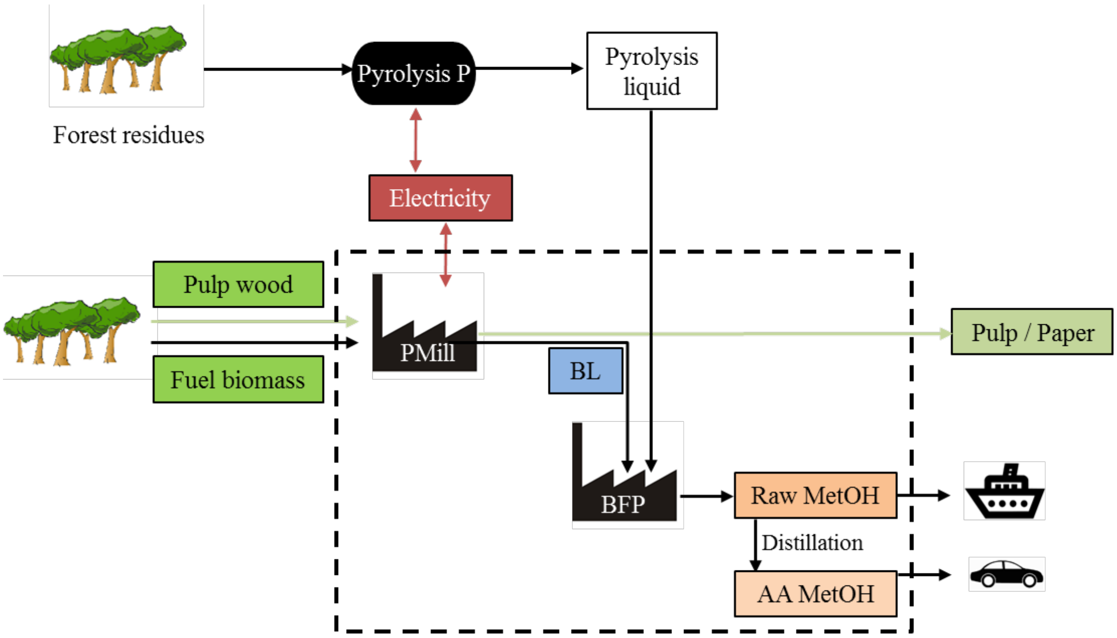
For logging residues, GHG emissions are considered from collection and transport in both RED and ISO calculations, and from changes in soil organic carbon stock only in ISO calculations. The GHG emissions data used for logging residues are 17.3 g CO_2-eq. kg^{-1} DM for collection and 42.2 g CO_2-eq. kg^{-1} DM for transport (Lindholm et al. 2010). Emissions from changes in soil organic carbon are assumed to be 179 g CO_2-eq. kg^{-1} DM, based on a scenario with two rotations (240 years) in northern Sweden (Lindholm et al. 2011). The same data for logging residues are used also for the fuel biomass input to the integrated pulp mill and biofuel plant, in all studied cases.

For co-gasification with black liquor, logging residues are converted through pyrolysis to pyrolysis liquid (Fig. 3.a). The pyrolysis process is assumed to take place in a stand-alone plant where 1 MJ of forest residues is assumed to require input of 32 J of electricity, and yield 0.6 MJ of pyrolysis liquid (at 29 % moisture content), which is based on modelling work at Luleå University of Technology (Zetterholm et al. 2018). The assumption of a stand-alone plant is in contrast to an integrated pyrolysis and CHP (combined heat and power) plant, where a higher total efficiency could be achieved (McKeough et al. 2005). Therefore a stand-alone plant could be considered a worst-case scenario for the design of the pyrolysis system, but here the less complex setup with a stand-alone pyrolysis plant is preferred as a base case.

In the cases of high blend (50 % mixture) of pyrolysis liquid to black liquor, sodium hydroxide (NaOH) is added to the blend with 12 kg NaOH per 100 kg of pyrolysis liquid. As a result of the NaOH addition, pyrolysis liquid makes up 46 % of the final mix, NaOH makes up 5.4 %, and black liquor 49 % (dry mass basis). The added salt is recovered together with the pulping chemicals in the BL, but for the calculations of GHG emissions, no recovery is assumed, and thus the calculations represent a worst case scenario regarding NaOH input for the process. For the GHG emissions calculations, 0.48 kg CO_2-eq. kg^{-1} NaOH is assumed (BioGrace 2012, updated GWP100 for methane).

For the reference cases, the alternative use of logging residues is considered to be direct gasification (Fig. 3.b), with downstream production of either crude or grade AA methanol. The mass and energy balances were based on process simulations (Carvalho et al. 2017b) and are presented in appendix (table A 5). Important modeling constraints were to produce a sufficient amount of process steam to meet the heat demands of the methanol plant as well as for the pre-treatment of the logging residues. Surplus heat was used to produce electricity via a condensing turbine. For each MJ input of logging residues, the downstream biofuel production via gasification yields approximately 0.66 MJ of methanol.

3.a) Co-gasification of BL and pyrolysis liquid from forest residues.



3.b) Alternative use of forest residues: direct gasification (Gas).

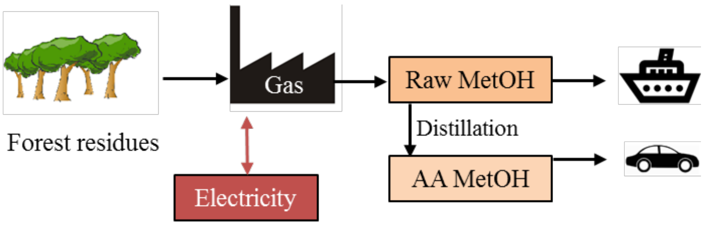


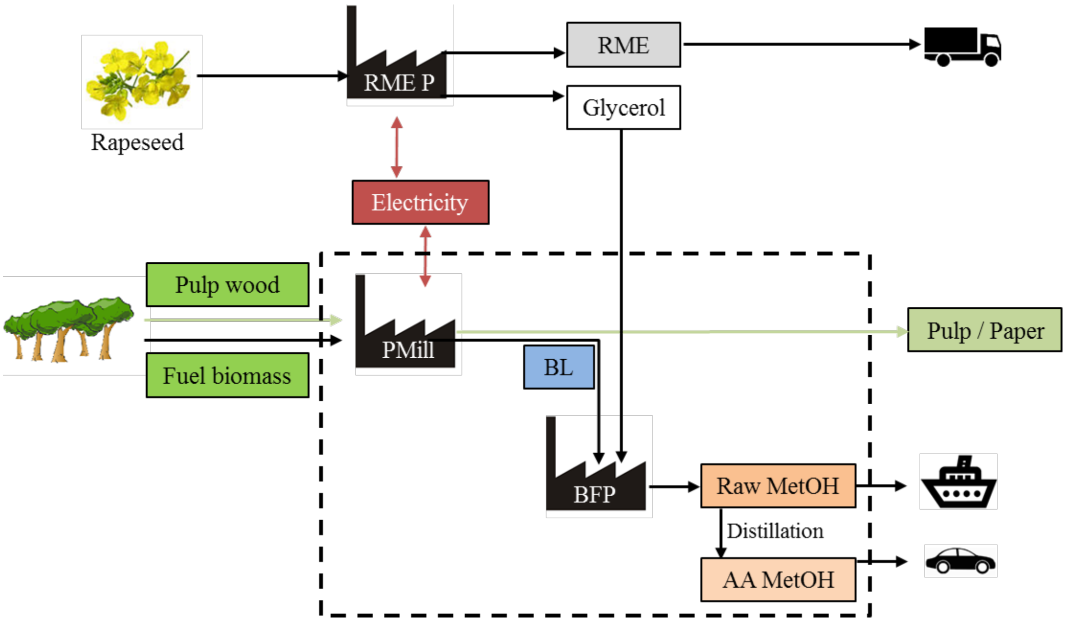
Figure 3. Schematic overview of the studied system for co-gasification of black liquor (BL) with pyrolysis liquid made from forest residues (3.a). In the reference case, the alternative use forest residues is direct gasification (Gas; 3.b).

2.1.3 Glycerol

The alternative use of glycerol considered is anaerobic digestion (Fig. 4.b), and the considered digestion process is based on assumptions of co-digestion with manure, and on general data for anaerobic digestion in a large size plant followed by upgrading of biogas to vehicle fuel. The assumed digestion of glycerol is thus based on a literature study, where the co-digestion with manure is important in order to assume that all necessary nutrients are available, and in order to avoid potential limitations to glycerol as a sole substrate.

The composition of crude glycerol is assumed to be (on a mass basis) 63 % glycerol, 0.4 % water, 31.6 % MONG (matter organic non glycerol) whereof 25 % FAME, and 5 % ash.

4.a) Co-gasification of BL and crude glycerol from RME plant (RME P).



4.b) Alternative use of crude glycerol: anaerobic digestion (AD).

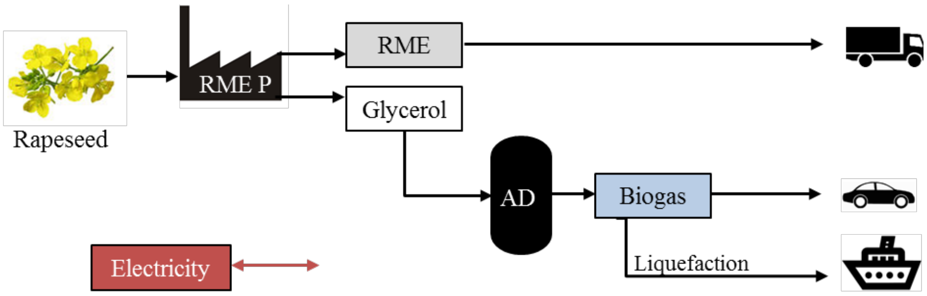


Figure 4. Schematic overview of the studied system for co-gasification of black liquor (BL) with crude glycerol from biodiesel (RME) production (4.a). In the reference case, the alternative use of crude glycerol is anaerobic digestion (AD; 4.b).

Anaerobic digestion

The chemical maximum methane yield from anaerobic digestion of crude glycerol is calculated theoretically using Buswell's formula, followed by assumptions for calculating a methane yield from the digestion process. For Buswell's formula, we assume that all fatty acids are oleic acid (18°C), resulting in 0.41 kg CH_4 per 1 kg crude glycerol digested. From the resulting chemical yield, we assume that [1/HRT] %, where HRT is the hydraulic retention time, of the substrate is short-circuited in the CSTR and thus is not digested. The HRT is assumed to be 25 days (based on Andriamanohiarisoamanana et al. 2016, Rodríguez-Abalde et al. 2017), meaning 1/HRT=4% of methane yield lost. Theoretically, 100 % of the remaining yield could be achieved if 100 % of the organic material is digested, but it is not practically achievable. For this study, we assume that 90 % of the organic material is digested[1]. Out of this material, another 5 % is assumed to be lost in the form of

---

[1] This assumption is important to decide the final amount of CH_4 fuel produced, but not important to the final GHG emissions from 1 MJ CH_4 fuel produced. This is because the methane slip from the plant and from the upgrading processes is calculated as a fraction of total methane produced, and therefore an increased methane

microorganism biomass, which results in a methane yield of 0.34 kg CH_4 per 1 kg crude glycerol. The final production of biogas and methane is estimated to 0.335 kg CH_4 per 1 kg crude glycerol, after subtracting methane slip from the digestion plant (0.5 % of produced methane), and methane slip from upgrading (1 % of methane to be upgraded) (Tufvesson et al. 2013).

The calculation of methane yield from anaerobic digestion of glycerol is based on the assumption that glycerol is co-digested with manure, in order to avoid potential inhibitory effects from the crude glycerol. In considering crude glycerol as a substrate for anaerobic digestion, the three main potentially inhibiting factors are considered to be i) intermediate products, ii) long fatty acids, and iii) inorganic salts (Viana et al. 2012). For i) the intermediate products, we assume a low blend and a continuous addition of glycerol, in order to avoid intermediary products accumulating to a critical level. Thus no inhibitory effect from intermediate products is considered. Regarding ii) long chain fatty acids, these come from the mono-, di- and triglycerides as well as FAME (RME) in the crude glycerol. In the reactor, the fatty acids separate from these molecules and can inhibit digestion. From this point of view, the ~25% of FAME in the considered crude glycerol is not beneficial, as it makes up most of the long fatty acid content. According to the literature, low concentrations cause inhibitory effects, and again, a low blend and continuous adding of glycerol is assumed to prevent the concentration from increasing. No inhibitory effect from long chain fatty acids is therefore considered, not ignoring the uncertainties of such an assumption. The third inhibitory factor considered is iii) inorganic salts. The considered crude glycerol appears to have relatively low contents of inorganic salts compared to values reported by literature as problematic (Viana et al. 2012), and also so here a dilution and continuous adding of glycerol is assumed to keep inorganic salts at acceptable levels. Thus no inhibitory effect from inorganic salts is considered. Conclusively, no inhibitory effects are considered since co-digestion with manure is assumed, but for the calculations of GHG emissions, only the part of digestion representing crude glycerol is included.

LCI data
The methane slip from the digestion plant and the upgrading process (water scrubber) is included in the calculation of GHG emissions. Furthermore, electricity and heat inputs are included: 7 kWh electricity and 25 kWh heat per ton of substrate (glycerol) and for the digestion plant, and 0.25 kWh electricity per Nm^3 biogas for the upgrading process (Tufvesson et al. 2013).

For the sensitivity analysis of including upstream GHG emissions for crude glycerol, corresponding to a share of GHG emissions from RME production, a mean value is derived from a study by (Börjesson and Tufvesson 2011). From the whole biofuel production system producing RME, the percentage of GHG emissions allocated to RME ranges from 61 % (energetic base) to 72 % (economic base), and 3 % is allocated to glycerol (energetic and economic bases). Here an allocation of 65 % to RME is used as average, with 3 % allocated to glycerol. Assuming total GHG emissions of RME to be 50 g CO_2-eq. MJ^{-1}, which can be considered a high emissions scenario based on unfertilized grassland as reference land use, a 3 % allocation to glycerol corresponds to 88 g CO_2-eq. kg^{-1} glycerol (using 38 MJ kg^{-1} for RME). If wheat cultivation were instead to be considered as the alternative land use, GHG emissions from RME would be cut by more than half to approximately 20 g CO_2-eq. MJ^{-1} RME, and the upstream impacts of glycerol would consequently follow. On the other hand, if the price for glycerol was to change, the allocation to glycerol using an economic basis would also change. For the purpose of this sensitivity analysis, only the value of 88 g CO_2-eq. kg^{-1} glycerol is used.

---

yield also results in increased methane slip. The two factors cancel each other out so that GHG emissions per MJ fuel produced are approximately the same irrespective of the fraction of organic material which is digested.

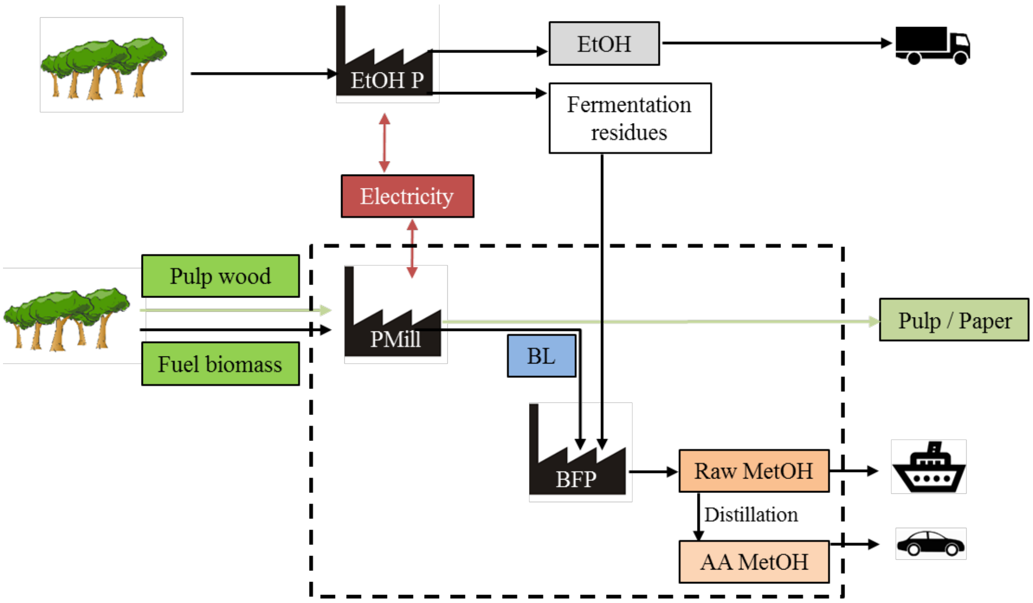
2.1.4 Fermentation residues

In the case of fermentation residues, the alternative use considered is combustion with power generation (Fig. 5.b). Thus the comparison of the end products, methanol in the co-gasification case as compared to methanol and electricity in the reference cases for black liquor and fermentation residues, respectively, does not fully follow the same logic as the other co-gasification cases. Nonetheless, since data for other conversion processes were not available in the current project, the combustion scenario allows for a comparative reference case for fermentation residues.

For the co-gasification of fermentation residues and black liquor (Fig. 5.a), sodium hydroxide (NaOH) is added to the blend with 0.2 kg NaOH per kg of fermentation residues. As a result, the low-blend (20%) mix finally consists of 3.8 % fermentation residues, 19 % NaOH, and 77 % black liquor (dry mass basis), and the high-blend (35%) mix consists of 6.5 % fermentation residues, 33 % NaOH, and 61 % black liquor. For the GHG emissions calculations, 0.48 kg CO_2-eq. kg^{-1} NaOH is assumed (BioGrace 2012, updated GWP100 for methane).

For the alternative use of fermentation residues for electricity generation, a conversion efficiency of 0.3 (based on Naturvårdsverket 2005) is used to estimate the amount of electricity generated from each energy unit of fermentation residues. The energy content of fermentation residues is 18 MJ kg^{-1} (80 % DM) and thus 1 kg of fermentation residues at 80 % DM yields 6 MJ of electricity. No additional energy inputs are considered. Notably, this scenario for fermentation residues is distinctly less elaborated as compared to the conversion alternatives for the other by-product feedstocks in this report. This is explained by the lack of suitable data for a biomass-to-biofuel conversion process for fermentation residues within this project.

5.a) Co-gasification of BL and fermentation residues from ethanol plant (EtOH P).



5.b) Alternative use of fermentation residues: combustion with power generation.

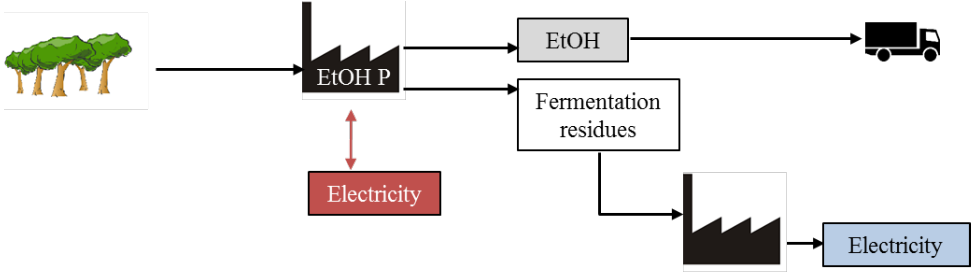


Figure 5. Schematic overview of the studied system for co-gasification of black liquor (BL) with fermentation residues from lignocellulosic ethanol production (5.a). In the reference case, the alternative use of fermentation residues is combustion with power generation (5.b).

3. Results and discussion

3.1 Black liquor and pyrolysis liquid

Comparing the co-gasification scenario to the reference scenario, Fig. 6 shows that more methanol is produced in the reference scenario, where black liquor and forest residues are gasified separately. Considering the loss in the additional conversion step in the co-gasification scenario – the pyrolysis process – this result is not unexpected, but it shows that the catalytic effect of black liquor in co-gasification does not fully compensate for the loss in the extra conversion step. The plant design could affect the efficiency to some extent, for instance the high blending ratio for co-gasification (50 % pyrolysis liquid) was not optimized in terms of overall plant efficiency. In addition, if the plant were integrated with CHP, a higher overall efficiency could potentially be achieved for all pyrolysis cases.

Regarding GHG emissions, results and conclusions vary. For the low-blend cases, the reference scenario results in slightly higher total GHG emissions (Fig. 7), but because the reference scenarios also produce more methanol, the GHG emissions per MJ of fuel are largely equal between scenarios. Using the RED calculation method (Fig. 7.a), GHG emissions are 10-11 g CO_2-eq. MJ^{-1}, and contrastingly, the results from the ISO method are 20-22 g CO_2-eq. MJ^{-1} (Fig. 7.b). For the high-blend cases, the GHG emissions per MJ of methanol are higher in the co-gasification cases than in the reference cases: 14-15 g CO_2-eq. MJ^{-1} (as compared to 9-10 g CO_2-eq. MJ^{-1}) using the RED method and approximately 32 g CO_2-eq. MJ^{-1} (as compared to 22 g CO_2-eq. MJ^{-1}) following the ISO method, but the difference in results would decrease if recycling of NaOH was considered. The RED method results in GHG emissions below the RED reduction target of 60 % reduction as compared to a fossil fuel reference (34 g CO_2-eq. MJ^{-1}), while the ISO results for the high-blend cases have emissions at that approximate level. From this comparison it is obvious that method choices are decisive to the total GHG emissions of the produced methanol, while the scenarios, including the comparison of grade AA or crude methanol, yield somewhat similar results.

Out of the total GHG emissions of the produced methanol, the main contributing processes are electricity for gasification and collection and transportation of forest residues. As an example of the uncertainty connected to the future scenario where the considered pulp mill and biofuel plant may be built, the electricity production in the Nordic countries could change, rendering the data for the Nordic electricity mix used in these calculations inaccurate. Therefore the final results of the calculations presented here should be viewed as a first screening results, and interpreted with caution.

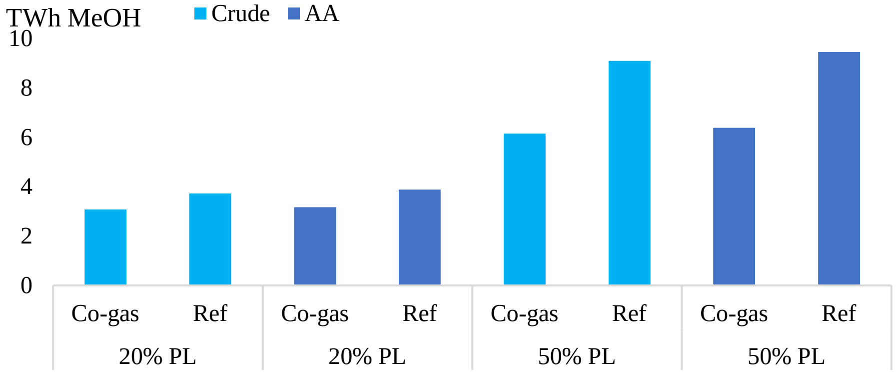


Figure 6. Co-gasification of black liquor and pyrolysis liquid: methanol (MeOH) fuel production from gasification and reference handling of the biomass. Indicated values correspond to yearly production.

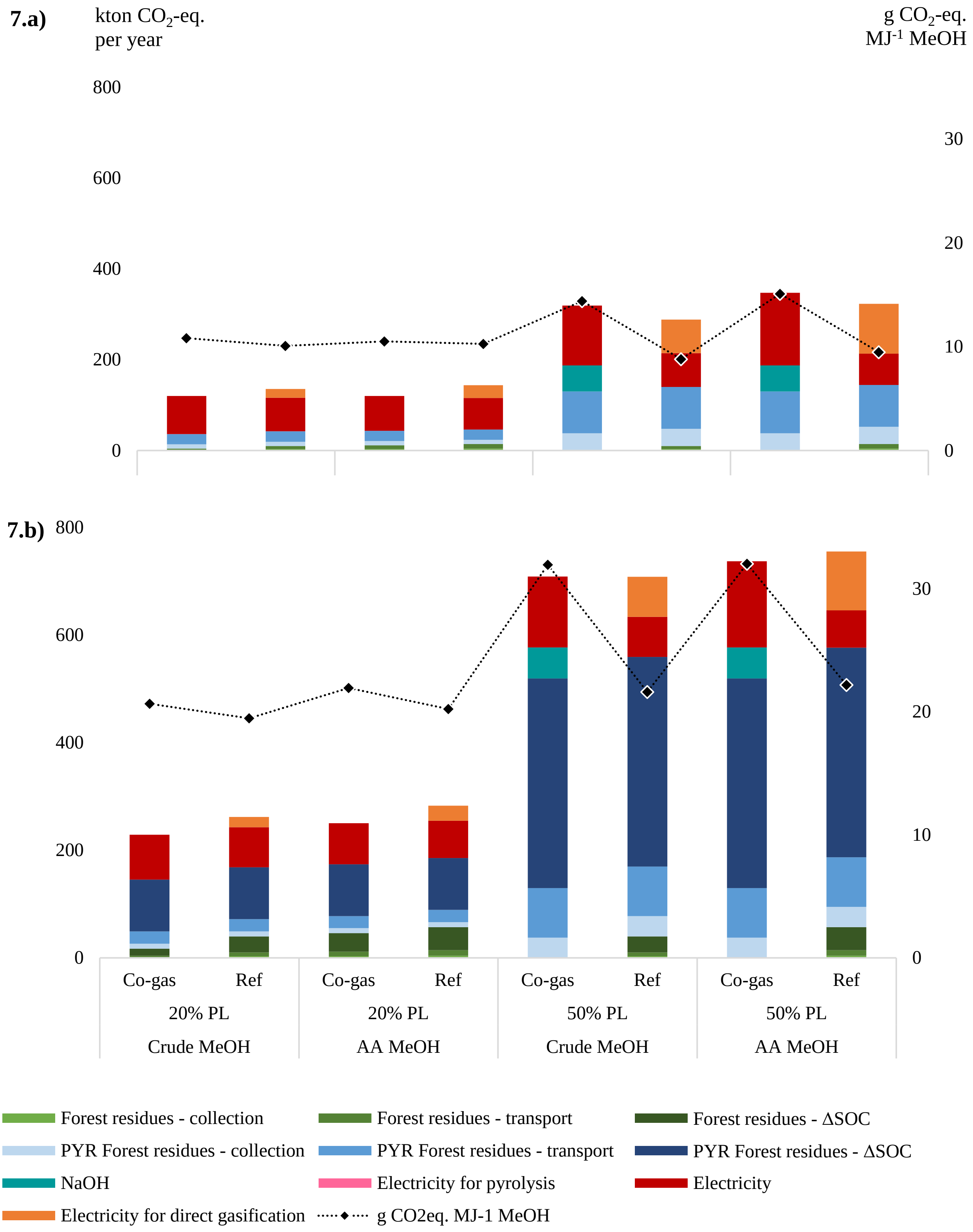


Figure 7. GHG emissions from co-gasification of black liquor and pyrolysis liquid, calculated following the RED method (7.a) and the ISO method (7.b).

3.2 Black liquor and glycerol

As can be seen in Fig. 8, the fuel production in terms of MWh (as methanol or methane fuel) is similar in the studied co-gasification and reference scenarios. While assumptions regarding the biogas yield from anaerobic digestion of crude glycerol are uncertain, the results show that both the co-gasification and reference conversion scenarios could yield similar amounts of transportation fuel in terms of energy content.

In terms of GHG emissions, both RED and ISO methods result in higher total GHG emissions for the reference scenarios (Fig 9). This in turn leads to higher GHG emissions from the fuels (methanol and methane) produced in the reference scenarios: 12 and 17 g CO_2-eq. MJ^{-1} calculated with RED and ISO methods, respectively, as compared to the methanol produced in the co-gasification scenarios: 5-8 and 10-12 g CO_2-eq. MJ^{-1} for RED and ISO calculations. Notably, the leakage of methane from the digestion scenario contributes significantly to the total GHG emissions of the reference scenarios, especially in the high-blend (50 % glycerol) cases. The actual methane slip varies between plants and practices, and the leakage from upgrading could potentially be reduced e.g. by oxidation of methane (Tufvesson et al. 2013). It is thus important to note that the resulting GHG emissions from the reference scenario could vary significantly with altered assumptions for methane slip. Still, the results show emissions below the current RED 60 % reduction target compared to a fossil fuel reference (34 g CO_2-eq. MJ^{-1}). No significant differences can be found in comparing the production of grade AA or crude methanol.

Also adding significantly to the total GHG emissions is electricity for gasification, and for the ISO results, upstream emissions of glycerol. Regarding GHG emissions from grid electricity, the same statement can be made for this co-gasification case as for the previous; the unknown future development of the energy system could find current assumptions inaccurate, and therefore, results should be interpreted with caution. Regarding upstream emissions of glycerol, the market situation for crude glycerol could affect what is considered a reasonable allocation to RME and glycerol respectively, and assumptions regarding rapeseed cultivation also affects the total GHG emissions to be considered. Considering that the current assumptions have a significant impact on the ISO results, upstream impacts should be taken into account when considering future uncertain scenarios for black liquor co-gasification with glycerol.

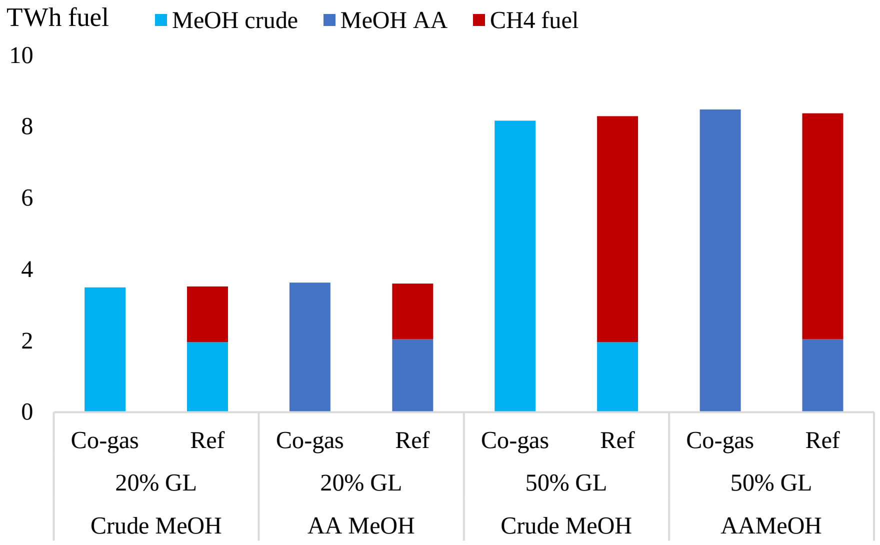


Figure 8. Co-gasification of black liquor and glycerol: production of methanol (MeOH) and methane (CH4) fuel from gasification and reference handling of the biomass. Indicated values correspond to yearly production.

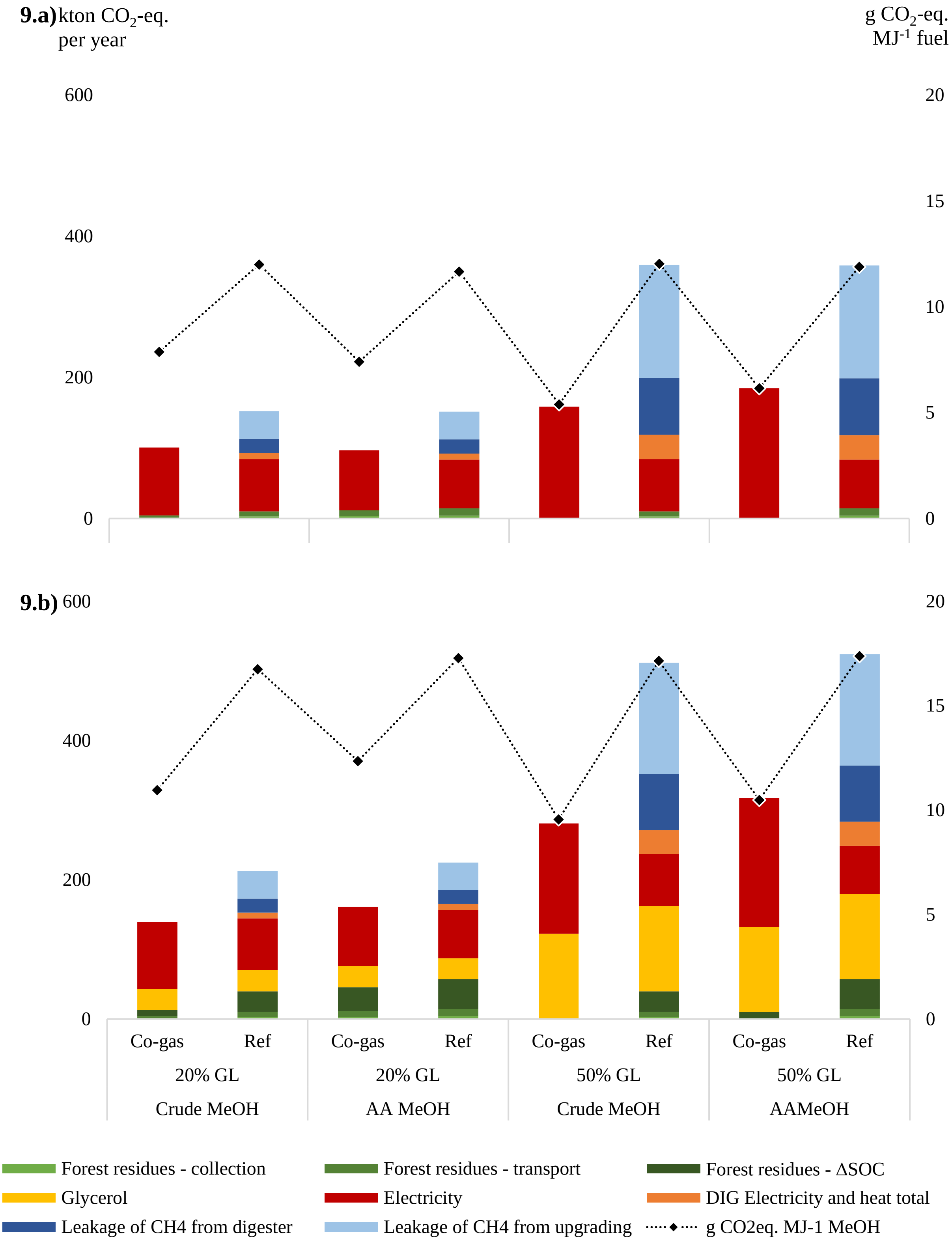


Figure 9. GHG emissions from co-gasification of black liquor and glycerol, calculated following the RED method (10.a) and the ISO method (10.b).

3.3 Black liquor and fermentation residues

As Fig. 10 shows, the co-gasification scenarios produce methanol while the reference scenario produces both methanol from black liquor gasification and electricity from combustion of fermentation residues. Due to the rather low conversion efficiency in power generation, the total energetic production is lower in the reference scenarios. However, the comparison of methanol as fuel to electricity is not straightforward, and thus further conclusions regarding the comparison of co-gasification and reference scenarios cannot be drawn here. The possibility that lignin-rich fermentation residues could be utilized in other technologies should also be acknowledged within this context, but nevertheless combustion serves the purpose of a comparative assessment.

The comparison of GHG emissions from the different scenarios vary depending on the calculation method used (Fig. 11). Using the RED calculation method, electricity for gasification is the main contributing process to the total GHG emissions (roughly 7-11 g CO_2-eq. MJ^{-1}) in all cases and scenarios, and the GHG emissions per MJ methanol or electricity produced are consequently slightly lower in the reference scenarios (Fig. 11.a). Contrastingly, results from the ISO method show changes in soil organic carbon as another important contributing process, and render the co-gasification and reference scenarios similar in terms of GHG emissions per MJ of methanol or electricity produced (roughly 10-14 g CO_2-eq. MJ^{-1}, Fig. 11.b). This aspect also affects the comparison of crude to grade AA methanol, where grade AA methanol results in slightly higher GHG emissions. Here, the method for calculation is decisive both to the final results in terms of total GHG emissions, and to the conclusion regarding comparison of co-gasification and reference handling. It is also worth noting that if recycling of NaOH in co-gasification was regarded, the difference in terms of GHG emissions between the co-gasification and reference cases would decrease.

With grid electricity being an important source for GHG emissions in all cases and scenarios, again, the future development of the energy system is decisive to the final GHG emissions from the studied systems. What has been said regarding the other studied systems is also valid here; results should be viewed as a first set of screening results, and interpreted with caution. With this in mind, it can be noted that the present results for methanol in the co-gasification scenario show emissions below the current RED 60 % reduction target compared to a fossil fuel reference (34 g CO_2-eq. MJ^{-1}).

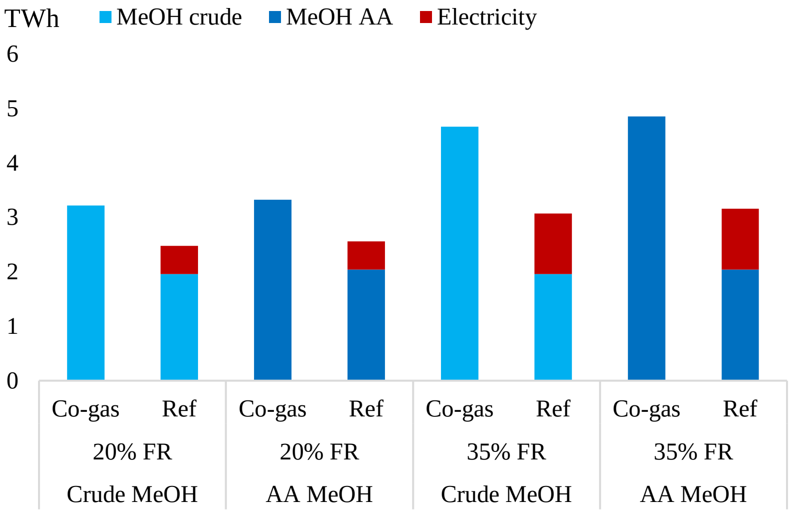


Figure 10. Co-gasification of black liquor and fermentation residues: production of methanol (MeOH) fuel and electricity from gasification and reference handling of the biomass. Indicated values correspond to yearly production.

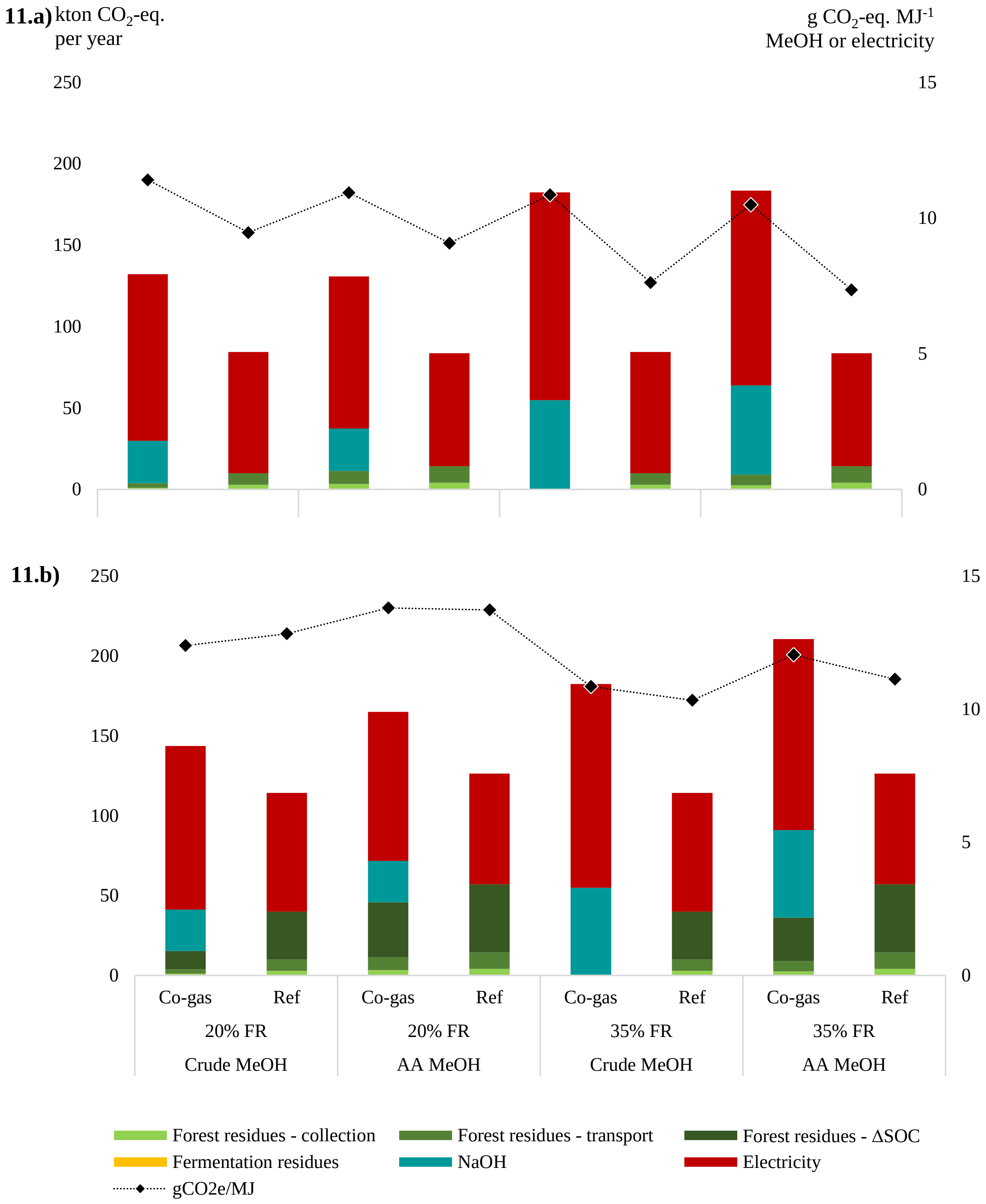


Figure 11. GHG emissions from co-gasification of black liquor and fermentation residues, calculated following the RED method (12.a) and the ISO method (12.b).

3.4 Common observations and uncertainty

Within each of the studied co-gasification systems, the method choices for calculating life-cycle GHG emissions largely influence the total GHG emissions of the fuels produced, and in the case of co-gasification of black liquor and fermentation residues, also the comparison between co-gasification and reference scenarios is affected. Using the RED method, the fuels studied in this report result in emissions savings of 82-94 % compared to the RED fossil fuel reference. By calculating GHG emissions following ISO standards, the results for the same fuels instead range from 62-88 % GHG emissions savings. Notably, the choice of calculation approach can affect the resulting GHG emissions significantly, and it should be noted that while the RED method results represent the current policy guidelines, they do not necessarily represent the most accurate GHG emissions of the studied fuel production systems. While the results from the RED method in this study meet the current policy goal of 60% reduction of GHG emissions as compared to a fossil reference, this should be re-evaluated with future policy changes. One such potential changed policy scenario is illustrated by the results following the ISO guidelines, where implications of including changes to soil organic carbon, and upstream GHG emissions of certain by-products, are presented. The assumption regarding upstream emissions of residual biomass could potentially be critical to results for residue-based products (Olofsson, 2017), and since the value of residual biomass is likely to increase in an expanded circular bioeconomy, this could motivate an increased allocation of the environmental impact of the main production systems also to the residual biomass streams. An example of including upstream GHG emissions has been shown here for glycerol, and future assessments should re-evaluate such assumptions.

As other examples of uncertainty connected to the presented results, the availability of resources should be noted, as also the design of the studied plants and systems. Firstly, the modelled co-gasification systems are based on the technical potential to blend by-product biomass into black liquor for co-gasification and methanol production in a future large-scale integrated pulp and biofuel plant. The future availability of the biomass resources has not been explicitly considered in this report and thus the feasibility of providing the required biomass has not been assessed. For instance, the availability of crude glycerol for co-gasification will depend both on the development of biodiesel production systems and on potential alternative uses of the glycerol. Because of this type of uncertainty, it is again important to note that the results presented in this study should be regarded as a first set of screening results for the studied technology. Secondly, regarding the plant and system design, this study has assessed one low-blend and one high-blend case for each considered by-product biomass co-gasification system, but the design of the integrated pulp mill and biofuel plant has not been optimized regarding final energy and emissions balances. Therefore the presented results could vary not only with current assumptions and data, but also with choice of the plant (and system) design.

In the light of uncertainties connected to future energy and resource scenarios, inventory data, and calculation approaches, the results presented here cannot carry decisive conclusions regarding the best use of the studied biomass resources from a GHG emissions or fuel production point of view. The studied by-product biomass materials can provide an increased resource base for methanol production through black-liquor co-gasification, but it appears that co-gasification does not provide any obvious benefits in terms of biomass to biofuel conversion efficiency and GHG emissions when compared to other potential conversion technologies. In order to further assess the potential of co-gasification as a potentially efficient route for biomass to biofuel conversion, better knowledge of the market development for and alternative handling of the studied biomass resources would be beneficial. Furthermore, as has been pointed out for each co-gasification system, the future development of electricity production will be decisive to results and conclusions as electricity use is an important contributor to the total GHG emissions. Generally, the difficulty in assessing non-existent large-scale technical systems brings uncertainty to the analysis presented in this work.

4. Conclusions

The present study shows that co-gasification of black liquor with an extended raw material base is comparable to alternative technologies in terms of biomass to biofuel conversion efficiency and GHG emissions. As such, the investigated by-product biomass resources could increase the raw material available for methanol production through co-gasification, but co-gasification does not appear to provide a more efficient biomass to biofuel conversion of said biomass resources when compared to alternative handling options. With GHG emissions calculated according to the EU RED method, all cases and scenarios fulfill the currently required 60 % GHG emissions reduction target (34 g CO_2-eq. MJ^{-1}) as compared to a fossil fuel reference.

The uncertainties connected to the present assessment are however significant, and the presented results should be regarded as a first screening results, and interpreted with caution. By calculating GHG emissions also according to the ISO standards' guidelines, the assessment shows that the final results are sensitive to method choices. Among the uncertain parameters are GHG emissions from the future energy system and electricity production, emissions due to removal of logging residues from the forest floor, upstream impacts of by-products, and the assumed alternative handling of by-product biomass resources. More exhaustive analyses with specific data and calculation considerations for each considered case would be needed in order to meet some of the uncertainties and to draw further conclusions.

References

Andriamanohiarisoamanana, F. J., Yamashiro, T., Ihara, I., Iwasaki, M., Nishida, T. and Umetsu, K. 2016. Farm-scale thermophilic co-digestion of dairy manure with a biodiesel byproduct in cold regions. *Energy Conversion and Management* 128: 273-280.

Bach Oller, A., Furusjö, E. and Umeki, K. 2015. Fuel conversion characteristics of black liquor and pyrolysis oil mixtures: Efficient gasification with inherent catalyst. *Biomass and Bioenergy* 79: 155-165.

Bugge, M., Hansen, T. and Klitkou, A. 2016. What Is the Bioeconomy? A Review of the Literature. *Sustainability*, 8: 691.

Börjesson, P. and Tufvesson, L. 2011. Agricultural crop-based biofuels – resource efficiency and environmental performance including direct land use changes. *Journal of Cleaner Production* 19(2): 108-120.

Carvalho, L., Lundgren, J., Wetterlund, E., Furusjö, E. and Wolf, J. 2017a. Techno-economic evaluation of black liquor gasification with expanded raw material base. Manuscript.

Carvalho, L., Furusjö, E., Kirtania, K., Wetterlund, E., Lundgren, J., Anheden, M. and Wolf, J. 2017b. Techno-economic assessment of catalytic gasification of biomass powders for methanol production. *Bioresource Technology* 237: 167-177.

ISO 2006a. Environmental management – Life cycle assessment – Principles and framework (ISO 14040:2006).

ISO 2006b. Environmental management - Life cycle assessment - Requirements and guidelines (ISO 14044:2006).

Keegan, D., Kretschmer, B., Elbersen, B. and Panoutsou, C. 2013. Cascading use: A systematic approach to biomass beyond the energy sector. *Biofuels, Bioproducts and Biorefining* 7(2): 193-206.

Lindholm, E.L., Berg, S. and Hansson, P.A. 2010. Energy efficiency and the environmental impact of harvesting stumps and logging residues. *European Journal of Forest Research* 129(6): 1223–1235.

Lindholm, E.L., Stendahl, J., Berg, S. and Hansson, P.A. 2011. Greenhouse gas balance of harvesting stumps and logging residues for energy in Sweden. *Scandinavian Journal of Forest Research* 26(6): 586-594.

Martinsson, F., J. Gode, J. Arnell and J. Höglund 2012. Emissionsfaktor för nordisk elproduktionsmix, PM För Energimyndigheten. IVL report B2118. Stockholm: IVL Svenska Miljöinstitutet.

McKeough, P., Solantausta, Y., Kyllönen, H., Faaij, A., Hamelinck, C., Wagener, M., Beckman, D. and Kjellström B. 2005. Techno-economic analysis of biotrade chain - Upgraded biofuels from Russia and Canada to the Netherlands. VTT Research Note 2312. Available at: http://www.vtt.fi/inf/pdf/tiedotteet/2005/T2312.pdf [2017-07-11]

Murray, A., Skene, K. and Haynes, K. 2015. The Circular Economy: An Interdisciplinary Exploration of the Concept and Application in a Global Context. *Journal of Business Ethics* 140(3): 369-380.

Myhre, G., Shindell, D., Bréon, F.M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T. and Zhang, H. 2013. Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (eds.)]. Cambridge and New York: Cambridge University Press.

Naturvårdsverket 2005. Förbränningsanläggningar för energiproduktion inklusive rökgaskondensering (utom avfallsförbränning). Branschfakta nr. 2. Stockholm: Naturvårdsverket.

Olofsson, J. and Börjesson, P. 2017. Residual biomass as resource – Life-cycle environmental impact of wastes in circular resource systems. Manuscript.

Renewable energy directive (2009/28/EC). Directive of the European Parliament and of the council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. L 140/16.

Rodríguez-Abalde, Á., Flotats, X. and Fernández, B. 2017. Optimization of the anaerobic co-digestion of pasteurized slaughterhouse waste, pig slurry and glycerine. *Waste Management* 61: 521-528.

SFS 2011:1088. Förordning om hållbarhetskriterier för biodrivmedel och flytande biobränslen. Stockholm: Miljö- och energidepartementet.

Swedish Energy Agency, 2012. Vägledning till regelverket om hållbarhetskriterier för biodrivmedel och flytande biobränslen. Version 3.0. ER 2012:27. Eskilstuna: Swedish Energy Agency.

Tufvesson, L., Lantz, M. and Björnsson, L. 2013. Miljönytta och samhällsekonomiskt värde vid produktion av biogas från gödsel. Rapport nr 86, Miljö och Energisystem, LTH, Lunds universitet. Available at: http://portal.research.lu.se/portal/en/publications/miljoenytta-och-samhallsekonomiskt-varde-vid-produktion-av-biogas-fraan-goedsel(f4321c82-f1fa-4319-ac1f-0694388245ea).html#Overview [2017-07-10]

Viana, M.B., Freitas, A.V., Leitão, R.C., Pinto, G.A.S. and Santaella, S.T. 2012. Anaerobic digestion of crude glycerol: a review. *Environmental Technology Reviews* 1(1): 81-92.

Zetterholm, J., Wetterlund, E., Pettersson, K. and Lundgren, J. 2018. Evaluation of value chain configurations for fast pyrolysis of lignocellulosic biomass: Integration, feedstock, and product choice. *Energy* 144: 564-575.

Appendix: Mass balances

The following sections, and tables A 1 to A 5, show the mass balances of the studied gasification systems. For each co-gasification case, 173.6 tons of black liquor (wet basis) is input to the biofuel plant hourly. The plant is assumed to run 8000 h per year.

Co-gasification of black liquor and pyrolysis liquid

Table A 1. Mass and energy balance for co-gasification of black liquor and pyrolysis liquid.

Co-gasification: black liquor and pyrolysis liquid						
			20% Pyrolysis liquid		**50% Pyrolysis liquid**	
		[Units]	**Crude MeOH**	**AA MeOH**	**Crude MeOH**	**AA MeOH**
Flows going IN	**Pulp wood**	**[t/h]**	107	107	107	107
		[MJ/kg]				
		ds [%]				
	Bark	**[t/h]db**	16	16	16	16
		[MJ/kg]db	19.56	19.56	19.56	19.56
		ds [%]				
	Fuel biomass	**[t/h]**	9	24	0	0
		[MJ/kg]ds	18.97	18.97	18.97	18.97
		ds [%]				
	Pyrolysis liquid	**[t/h]ar**	43	43	174	174
		[MJ/kg]	17.41	17.41	17.41	17.41
		ds [%]	75	75	75	75
	NaOH	**[t/h]ar**	x	x	20	20
		water [%]	x	x	25	25
	Electricity	**[MW]el**	104	95	131	159
Flows going OUT	**Electricity**	**[MW]el**	0	0	0	0
	Pulp	**[Adt/h]**	82	82	82	82
	Raw MeOH	**[t/h]**	66	x	132	x
		[MJ/kg]	21	x	21	x
	AA MeOH	**[t/h]**	x	62	x	125
		[MJ/kg]	x	23	x	23
	Hot water	**[t/h]**	1323	1323	2596	2596
		[°C]	95	95	95	95

Co-gasification of black liquor and glycerol

Table A 2. Mass and energy balance for co-gasification of black liquor and glycerol.

Co-gasification: black liquor and glycerol						
			20% Glycerol		**50% Glycerol**	
		[Units]	**Crude MeOH**	**AA MeOH**	**Crude MeOH**	**AA MeOH**
Flows going IN	**Pulp wood**	**[t/h]**	107	107	107	107
		[MJ/kg]				
		ds [%]				
	Bark	**[t/h]db**	16	16	16	16
		[MJ/kg]db	19.56	19.56	19.56	19.56
		ds [%]				
	Fuel biomass	**[t/h]**	6	24	0	7
		[MJ/kg]	18.97	18.97	18.97	18.97
		ds [%]				
	Glycerol	**[t/h]ar**	43	43	174	174
		[MJ/kg]				
		ds [%]	99.6	99.6	99.6	99.6
	Electricity	**[MW]**	96	85	158	184
Flows going OUT	**Electricity**	**[MW]el**	0	0	0	0
	Pulp	**[Adt/h]**	82	82	82	82
	Raw MeOH	**[t/h]**	75	x	175	x
		[MJ/kg]	21	x	21	x
	AA MeOH	**[t/h]**	x	71	x	166
		[MJ/kg]	x	23	x	23
	Hot water	**[t/h]**	1402	1402	2999	2999
		[°C]	95	95	95	95

Co-gasification of black liquor and fermentation residues

Table A 3. Mass and energy balance for co-gasification of black liquor and fermentation residues.

Co-gasification: black liquor and fermentation residues						
			20% Fermentation residues		**35% Fermentation residues**	
		[Units]	**Crude MeOH**	**AA MeOH**	**Crude MeOH**	**AA MeOH**
Flows going IN	**Pulp wood**	**[t/h]**	107	107	107	107
		[MJ/kg]				
		ds [%]				
	Bark	**[t/h]db**	16	16	16	16
		[MJ/kg]db	19.56	19.56	19.56	19.56
		ds [%]				
	Fuel biomass	**[t/h]**	8	24	0	19
		[MJ/kg]	18.97	18.97	18.97	18.97
		ds [%]				
	FR	**[t/h]ar**	43	43	93	93
		[MJ/kg]	19.33	19.33	19.33	19.33
		ds [%]	80	80	80	80
	NaOH	**[t/h]ar**	9	9	19	19
		Water [%]	20	20	20	20
	Electricity	**[MW]**	102	93	127	119
Flows going OUT	**Electricity**	**[MW]el**	0	0	0	0
	Pulp	**[Adt/h]**	82	82	82	82
	Raw MeOH	**[t/h]**	69	x	100	x
		[MJ/kg]	21	x	21	x
	AA MeOH	**[t/h]**	x	65	x	95
		[MJ/kg]	x	23	x	23
	Hot water	**[t/h]**	1330	1330	1861	1861
		[°C]	95	95	95	95
	Extra LPS	**[t/h]**	0	0	16	6

Gasification of black liquor (reference case)

For each case, 174 tons of black liquor (DM) is input to the system, producing either crude or grade AA methanol.

Table A 4. Mass and energy balance for gasification of black liquor.

Black liquor gasification (reference)				
		[Units]	**Crude MeOH**	**AA MeOH**
Flows going IN	**Pulp wood**	**[t/h]**	107	107
		[MJ/kg]		
		ds [%]		
	Bark	**[t/h]db**	16	16
		[MJ/kg]db	19.56	19.56
		ds [%]		
	Fuel biomass	**[t/h]**	21	30
		[MJ/kg]ds	18.97	18.97
		ds [%]		
	Electricity	**[MW]el**	74	69
Flows going OUT	**Electricity**	**[MW]el**	0	0
	Pulp	**[Adt/h]**	82	82
	Raw MeOH	**[t/h]**	42	x
		[MJ/kg]	21	x
	AA MeOH	**[t/h]**	x	40
		[MJ/kg]	x	23
	Hot water	**[t/h]**	867	867
		[°C]	95	95

Direct gasification of logging residues (reference case)

Table A 5. Mass and energy balance for direct gasification of logging residues.

Gasification of logging residues (reference case)						
			Corresponding to 20 % PL case		**Corresponding to 50 % PL case**	
		[Units]	**Crude MeOH**	**AA MeOH**	**Crude MeOH**	**AA MeOH**
	Fuel biomass	**[t/h]**	64	64	257	257
		[MJ/kg]ds				
		ds [%]	100	100	100	100
	Electricity	**[MW]el**	19	28	74	109
Flows going OUT	**Electricity**	**[MW]el**	0	0	0	0
	Raw MeOH	**[t/h]**	38	x	153	x
		[MJ/kg]	21	x	21	x
	AA MeOH	**[t/h]**	x	36	x	145
		[MJ/kg]	x	23	x	23
	Hot water	**[t/h]**	304	304	1230	1230
		[°C]	95	95	95	95