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Energy conversion performance of black liquor gasification to hydrogen production using direct causticization with CO_2 capture

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ABSTRACT

This paper estimates potential hydrogen production via dry black liquor gasification system with direct causticization integrated with a reference pulp mill. The advantage of using direct causticization is elimination of energy intensive lime kiln. Pressure swing adsorption is integrated in the carbon capture process for hydrogen upgrading. The energy conversion performance of the integrated system is compared with other bio-fuel alternatives and evaluated based on system performance indicators. The results indicated a significant hydrogen production potential (about 141 MW) with an energy ratio of about 0.74 from the reference black liquor capacity (about 243.5 MW) and extra biomass import (about 50 MW) to compensate total energy deficit. About 867,000 tonnes of CO_2 abatement per year is estimated i.e. combining CO_2 capture and CO_2 offset from hydrogen replacing motor gasoline. The hydrogen production offers a substantial motor fuel replacement especially in regions with large pulp and paper industry e.g. about 63% of domestic gasoline replacement in Sweden.

1. Introduction

1.1. Background

There is a worldwide interest growing to convert biomass e.g. forestry and agricultural residues, into renewable fuels, electricity or chemicals of higher value. Being renewable, biomass-based fuels have significant benefits in terms of environment and sustainability i.e. zero CO_2 emissions reducing global warming. As per European Union (EU) renewable directive 2009, there shall be a 20% share of renewable sources in energy supplied in EU by 2020 and a considerable share of 10% bio-fuels in transport sector (Kåberger et al., 2009). Several fuel producing options exist from biomass gasification using synthesis gas generated from gasification technology including methanol, dimethyl ether (DME), hydrogen, Fischer–Tropsch fuels, and synthetic natural gas. Hydrogen is considered as a promising energy carrier that can be used in vehicle fuel cells and internal combustion (IC) engines. One significant advantage of using hydrogen as a transport fuel is that almost all internal combustion (IC) engines in current automobiles could be converted to burn hydrogen emitting only water vapors without CO_2 emissions. Electricity could be generated from hydrogen fuel cells in power plants with high efficiency. However, the cost to run a hydrogen fuel vehicle is high since it requires a substantial amount of energy to store or to liquefy hydrogen. This limitation could be overcome to some extent by using compressed hydrogen gas identical to compressed natural gas (CNG). The distribution of hydrogen to vehicles could require changes in the fuel distribution network as well as modification in gasoline-fuelled vehicles.

Currently about 95% of the hydrogen production comes from fossil resources used as raw material for petrochemical, food and electronic industries (Thomas et al., 2002). Alternative hydrogen production technologies must be developed identifying most energy efficient route in terms of sustainability, efficiency, cost effectiveness, and safety, to meet global growing hydrogen demand. However, with increasing hydrogen demand for zero-emission energy products, the use of biomass in future energy systems is significantly important.

Pulp and paper industry consumes a large proportion of biomass worldwide that include bark, wood residues, and black liquor. Biorefinery operations to generate power, renewable fuels or chemicals can be integrated with modern pulp mills having established infrastructure for handling and processing biomass. In regions with large pulp and paper industry, black liquor (BL) is considered as a major energy source that can be gasified to produce synthesis gas producing various valuable energy products in downstream processes. In addition, black liquor gasification (BLG) has potential to replace conventional black liquor recovery system with the recovery boiler. The recovery boiler (RB) technology is in use for several decades but it has several disadvantages e.g. low electric power generation efficiency, smelt-water explosions and reduced-sulfur gas emissions (Larson et al., 2006; Whitty, 2005).

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Nomenclature

ADt	air dried tonnes
ASU	air separation unit
BFW	boiler feed water
BL	black liquor
BLG	black liquor gasification
BLS	black liquor solids
CBLG	Chemrec black liquor gasification
CCS	carbon capture and storage
CFB	circulating fluidized bed
CHP	combined heat and power
DARS	direct alkali regeneration system
DBLG	dry black liquor gasification
DME	dimethyl ether
EU	European Union
FAO	Food and Agriculture Organization
HTS	high temperature shift
IC	internal combustion
KAM	Kretslopps Anpassad Massafabrik
LHV	lower heating value
LTS	low temperature shift
MeOH	methanol
MTCI	Manufacturing and technology conversion international
MW	mega watt = 10^6 watt
PSA	pressure swing adsorption
RB	recovery boiler
SNG	synthetic natural gas
TWh	terawatt hour = 10^{12} watt hour

1.2. Previous studies

A number of studies investigated different black liquor gasification technologies to replace conventional black liquor recovery cycle e.g. SCA-Billerud process, DARS process, MTCI process, black liquor gasification with direct causticization, and Chemrec process (Andersson and Harvey, 2007; Berglin and Berntsson, 1998; Dahlquist and Jacobs, 1994; Dahlquist and Jones, 2005; Ekbom et al., 2003). The performance of BLG based combined heat and power (CHP) integrated with the KAM reference mill, an Eco-cyclic pulp mill research programme (see KAM report, 2003) was studied (Maunsbach et al., 2001). Preliminary economics of BLG based methanol and DME production was assessed (Berglin et al., 2002). The black liquor gasification based bio-refinery operations for bio-fuel production e.g. DME, Fischer–Tropsch liquids, and ethanol-rich mixed-alcohols was studied (Consonni et al., 2009). CO_2 mitigation technologies integrated with pulp and paper mills was evaluated (Joelsson and Gustavsson, 2008; Möllersten et al., 2003a,b; Yan et al., 2007). A catalytic hydrothermal gasification route to produce methane from woody biomass was presented (Luterbacher et al., 2009; Sricharoenchaikul, 2009; Waldner and Vogel, 2005).

1.3. Motivation and objective

Most of the studies focused on potential of electricity or bio-fuel production with pressurized thermal BLG system integrated with modern pulp mills. The present paper is a continuation of previous work to identify most efficient bio-fuel route from different BLG technologies e.g. pressurized Chemrec gasification for dimethyl ether and methanol production, catalytic hydrothermal gasification for direct methane production, and dry BLG for synthetic natural gas, based on various system performance (Naqvi et al., 2010a, 2010b, 2010c, 2012a,b). The indicators i.e. material and energy balances, potential black liquor to hydrogen production, energy efficiency, and potential CO_2 reductions, are chosen because these are the major drivers of converting a conventional pulp and paper mill into a bio-refinery. These performance indicators should give substantially better and competitive results of integrated black liquor gasification based bio-fuel production compared to the conventional black liquor recovery system for a successful commercialization. In addition, the competitiveness of hydrogen production is evaluated using 'system performance indicators' by comparing overall process energy efficiency with other bio-fuel alternatives from integrated BLG.

The purpose of this article is to investigate hydrogen production potential from a circulating fluidized bed black liquor gasification system with the direct causticization and system integration with the reference pulp mill that produces about 1000 air dried tonnes (ADt) per day of pulp. Pressure swing adsorption is employed as a carbon capture technology with hydrogen upgrading from the synthesis gas achieving potential negative-CO_2 emissions. The emphasis of the study is to avoid any major impact on the conventional pulping process recovering cooking chemicals for re-use during delignification.

2. Black liquor to hydrogen: System configuration

Black liquor is spent cooking liquor that contains organics from the wood (lignin) and the in-organic chemicals used for the delignification. A typical pulp and paper mill uses a large amount of in-organic chemicals and it is environmentally and economically desirable to recover these chemicals. The in-organic part (about 45% mass of the black liquor as dry) mainly consists of sodium carbonate and sodium sulfate (Dahlquist and Jones, 2005). The remaining part (about 55% mass of the black liquor as dry) is organic which is gasified to produce the synthesis gas. Due to presence of the in-organic materials, the lower heating value (LHV) per tonne of black liquor solids is relatively low (LHV, 12.3 MJ/kg). In a BLG system, black liquor is gasified at high temperatures in a reactor and the in-organic content is separated from the synthesis gas. Black liquor conversion to hydrogen completes in three major process steps, (i) circulating fluidized bed gasification with direct causticization, (ii) CO-shift, and (iii) the synthesis gas upgrading with CO_2 capture.

2.1. Air separation unit

The black liquor gasifier is fed with nearly pure oxygen (about 99% concentration) as gasifying medium to avoid high concentration of nitrogen in the synthesis gas. For this reason, a simple cryogenic air separation unit is used. However, for commercial process this high quality oxygen is not required, but a cryogenic air separation unit is selected as the most common process for air separation used by majority of industries meaning that the real process can be cheaper and less complicated.

2.2. Dry BLG with direct causticization

A dry BLG (DBLG) system with direct causticization replaces the conventional recovery boiler with a circulating fluidized bed (CFB) gasifier (i.e. titanium dioxide (TiO_2) as bed material). The name 'dry' given to the gasification technology is based on the fact that the black liquor is gasified at 800 °C which is below the melting