Applied Energy 90 (2012) 24–31

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Bio-refinery system in a pulp mill for methanol production with comparison of pressurized black liquor gasification and dry gasification using direct causticization

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ARTICLE INFO

Article history:
Received 21 September 2010
Received in revised form 20 December 2010
Accepted 27 December 2010
Available online 26 January 2011

Keywords:
Bio-fuel
Bio-refinery
Black liquor gasification
Methanol
Pulp mill

ABSTRACT

Black liquor gasification (BLG) for bio-fuel or electricity production at the modern pulp mills is a field in continuous evolution and the efforts are considerably driven by the climate change, fuel security, and renewable energy. This paper evaluates and compares two BLG systems for methanol production: (i) oxygen blown pressurized thermal BLG; and (ii) dry BLG with direct causticization, which have been regarded as the most potential technology candidates for the future deployment. A key objective is to assess integration possibilities of BLG technologies with the reference Kraft pulp mill producing 1000 air dried tonnes (ADt) pulp/day replacing conventional recovery cycle. The study was performed to compare the systems' performance in terms of potential methanol production, energy efficiency, and potential CO_2 reductions. The results indicate larger potential of black liquor conversion to methanol from the pressurized BLG system (about 77 million tonnes/year of methanol) than the dry BLG system (about 30 million tonnes/year of methanol) utilizing identical amount of black liquor available worldwide (220 million tDS/year). The potential CO_2 emissions reduction from the transport sector is substantially higher in pressurized BLG system (117 million tonnes/year CO_2 reductions) as compared to dry BLG system (45 million tonnes/year CO_2 reductions). However, the dry BLG system with direct causticization shows better results when considering consequences of additional biomass import. In addition, comparison of methanol production via BLG with other bio-refinery products, e.g. hydrogen, dimethyl ether (DME) and bio-methane, has also been discussed.

1. Introduction

Pulp and paper industry consumes a large proportion of biomass worldwide that include bark, wood residues, and black liquor (BL). Being a limited resource, biomass must be used as efficiently as possible. Due to the fact that modern pulp and paper industries have established infrastructure for handling and processing biomass, it is possible to lay foundation for future gasification based bio-refineries to co-produce electricity, chemicals or bio-fuels with pulp and paper products. There is potential to export electricity or bio-fuels by improving today's existing pulp and paper mills.

Black liquor is a major bio-energy resource, especially in countries having large pulp and paper industry. Black liquor is the residue of lignin and spent chemicals produced during chemical pulping process in digesters, also known as Kraft process. In conventional pulp mills, black liquor is fired in a recovery boiler (RB) to produce steam and electricity and to recover cooking chemicals for re-use in the digestion unit. The recovery boiler technology has proven to work well but it has several major disadvantages in terms of low electric power generation efficiency, risk of smelt-water explosions and reduced-sulfur gas emissions [1,2]. There has been a significant interest in developing new technologies like BLG to avoid such drawbacks associated with the conventional recovery boilers.

Several concerted efforts have been made in recent years to evaluate energy consequences of the integrated BLG technology in the pulp mills and to compare utilization of black liquor in the most efficient manner [3–8]. Mass and energy balances for a conventional pulp mill with the recovery boiler are compared with a pulp mill integrated BLG plant to investigate energy, environmental and economic consequences [9,10]. Integration of BLG with advanced gas turbine has been studied by Maunsbach et al. [12] within an eco-cyclic pulp mill research program (see KAM report, 2003 for an overview) [11], to improve the performance of the combined heat and power. The advanced gas turbines include evaporative gas turbine (EvGT) [13] and externally fired gas turbine (EFGT) [14–17]. Berglin et al. assessed the preliminary

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doi:10.1016/j.apenergy.2010.12.074

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
DARS	direct alkali regeneration system
DBLG	dry black liquor gasification
DME	dimethyl ether
FAO	food and agriculture organization
KAM	kretslopps anpassad massafabrik
LHV	lower heating value
MeOH	methanol
RB	recovery boiler

economics of BLG with motor fuel production, e.g. methanol and dimethyl ether (DME) [18]. Andersson and Harvey analyzed pulp mill integrated hydrogen production from BLG and compared with stand-alone hydrogen production from biomass gasification [19,20]. Consonni et al. studied gasification based bio-refinery operations for bio-fuel production, e.g. DME, Fischer–Tropsch liquids, and ethanol-rich mixed-alcohols [21]. Naqvi et al. investigated two different BLG technologies, i.e. pressurized gasification for DME production and catalytic hydrothermal gasification for methane production [22]. A number of studies presented dry BLG technology with direct causticization. Equilibrium calculations were performed on direct causticization with titanium dioxide (TiO_2) using a program called FACT [23]. Zeng and Heiningen carried out experimental tests in a fluidized bed reactor processing 1 kg of dry black liquor solids (BLS) per hour [24]. Richards et al. [25] and later Nohlgren and Sinquefield [26] have done complimentary investigations on causticization chemistry. From the results of various studies and experiences from pilot plant, it is believed that if important technical issues are resolved, commercialization of BLG technology will be reached within a decade [27].

The potential of electricity or bio-fuel production have been studied mostly with pressurized BLG system integrated with modern pulp mills but there is no valuable effort made to estimate the potential electricity or bio-fuel production from other gasification technologies. The aim of the study is to investigate energy conversion performance of black liquor to methanol production comparing two different types of BLG technologies: (i) oxygen blown pressurized entrained flow gasification (Chemrec design), and (ii) dry black liquor gasification process with direct causticization. The emphasis is to keep the pulping process unchanged without any major impacts and recover all cooking chemicals from black liquor to re-use in digestion unit. The energy withdrawn in terms of black liquor conversion to methanol must be compensated by additional biomass import. Fig. 1 shows bio-refinery concept in the integrated pulp mill with BLG to replace conventional recovery boiler. System performance is analyzed in terms of potential methanol production, overall system efficiency (i.e. energy ratios and black liquor to methanol efficiency), and comparison of methanol production route with other possible bio-refinery alternatives, e.g. H_2, DME and CH_4. In addition, the potential CO_2 reductions are estimated if methanol is used as an automotive fuel replacing fossil gasoline.

2. Pulping and BLG processes

2.1. Conventional pulping process

The dominant pulp production process is chemical pulping process, also known as Kraft process, in which the cellulose fibers are separated from the lignin. The process includes a major operation known as digestion where wood chips are impregnated with the cooking liquor. The wood chips are cooked at a temperature of 150–170 °C under highly alkaline conditions in the presence of sulfide [11]. The produced pulp is washed to recover black liquor and reduce the carryover of organic component in oxygen delignification unit. The pulp is then bleached with chlorine dioxide and hydrogen peroxide in a sequence of acidic and alkaline stages. The bleached pulp is dried with hot air before shipped to paper mills.

From the energy perspective, a modern Kraft pulp mill is self sufficient thanks to the black liquor recovery cycle: all internal steam and electricity demand can be met by recovering energy from the dissolved lignin in the black liquor [10]. The conventional recovery boilers are employed for dual purposes, i.e. recover energy and cooking chemicals from black liquor. Due to the presence of high organic content from the dissolved lignin; black liquor represents a potential energy source of 250–500 MW per mill that

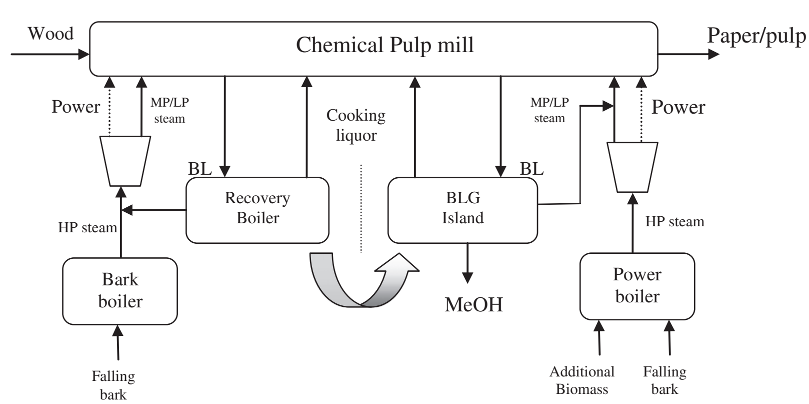

Fig. 1. Concept of bio-refinery system in the integrated pulp mill with BLG replacing the recovery boiler.