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STUDY ON THE PROCESS OF GASIFICATION OF BLACK LIQUOR

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Abstract
This review paper describes the potential of developing a new lignocellulosic biorefinery concept integrated with the Kraft industry. To demonstrate that gasification is a sustainable and more valuable processing route than burning it in recovery boilers, additional processes of syngas cleaning and high sulfur recovery are required in order to achieve a significant reduction in operating costs to improve economic feasibility through BL gasification. BL gasification is performed using two types of gasifiers, one with a fluidized bed, which requires a higher air velocity to increase the yield of valuable products aiding to increase the calorific value of the produced gas compared to fixed bed gasifiers. Fixed-bed gasifiers produce gas with a high tar content because the heat and mass transfer between the gasifier and the biomass is low and non-uniform. BL gasification offers great potential for increased energy recovery with a reduced amount of emissions compared to that of conventional BL burning in recovery boilers.

Keywords: black liquor, fluidized bed gasifier, fixed bed gasifier, syngas.

1. INTRODUCTION

According to the results stated during the last edition of National Inventory of Greenhouse Gases (NGHGI 2022) and published by the UNFCCC, all industrial sectors such as Energy, Industry, Agriculture, LULUCF (Land Use, Land-Use Change and Forestry) generate waste in an overwhelming proportion. Currently, 85 % of the world's energy comes from burning fossil fuels, but the use of renewable sources is still expected to expand by 50 % from 2001 to 2040, as shown in **Table 1**. In 2020, the world's total energy consumption was estimated at 560 exajoules (EJ), which is to be expected to increase at 712 EJ in 2040, according to International Energy Agency statistics (Shahabuddin and Alam, 2022). The huge consumption of energy worldwide is expected to generate negative impacts, such as: global warming, droughts, floods that lead to the depletion of non-renewable resources. This global situation encourages researchers to develop new technologies that use clean and renewable sources, including increasing the production of biofuels, as one of the possible solutions to the problems in the agricultural and transport sectors.

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Table 1. ***The world's primary renewable sources of energy*** *(Hoque and Rashid, 2021)*

Source	**Year**				
	2001	**2010**	**2020**	**2030**	**2040**
Biomass MWh	1080	1313	1791	2483	3271
Solar MW	4.10	15.0	66.0	244.0	480.0
Hydropower MW	22.70	266.0	309.0	341.0	358.0
Wind MW	4.70	44.0	566.0	542.0	688.0
Tidal/wave	0.050	0.10	0.40	3.0	20.0
Geothermal	43.20	86.0	186.0	333.0	493.0
Total energy consumption	10.038	10.549	11.425	12.352	13.310

At the level of the European Union (EU), less than 24 % of the energy requirement is provided by renewable sources, biomass, wind, fuel cells and waste. These results, correlated with the predicted forecasts and the serious problem of global warming, require finding urgent solutions for the large-scale production of energy from renewable sources (Hruška et al., 2020). Biomass is a known alternative source of clean energy that is still not being used to its full potential (Sonjaya et al., 2023). In the recent years, studies on new energy resources have focused on economic, environmental and social aspects, their purpose being the valorization of plastic waste, due to the majority content in energy elements, C and H, but the applied methods had a negative ecological impact. More than 50 million tons of post-consumer plastic waste are produced annually in the USA, Japan and EU. The disposal of plastic waste is a significant problem and for this reason many studies have been carried out on the recovery of different types of plastics through gasification and pyrolysis processes to produce gases and liquid valuable products. The process of gasification of plastic waste takes place under air conditions in the thermal range 800-1000 °C, and under oxygen for temperatures in the range 1000 - 1500 °C (Shah et al., 2022). The technology of hydrogen production through biomass gasification has become a topical direction in this field, as a result of low processing costs. The development and widespread use of biofuels of various types have been identified as the key to success in the pulp and paper industry (Guomin et al., 2022). Biomass gasification is a common process for the production of biofuels, proving commercial progress especially in the last decade. The waste called black liquor (BL) resulting in the pulp and paper industry can also be used for the production of syngas and for the further development of biofuels (Yawer et.al., 2016). BL product gasification is of interest to both chemical engineers, academics, as well as paper mill operators and entrepreneurs, who want to apply solutions that protect the environment, viable and economically efficient (Bajpai, 2014). In this study, a description of BL as a biomass resource is provided based on its application to optimize the production conditions of gaseous products, hydrogen and methane, in addition, the cost of black liquor gasification is approximately $ 0.06 per kg. Liquid and gaseous products from gasification could be obtained at a cost of $ 56.64 and $ 3.35 per ton of stream, respectively. Therefore, black liquor gasification is an interesting challenge for obtaining fuel gases and value-added bioproducts (Barros et al., 2022). The in situ gasification experiment included the following parameters: temperature of 1173 K, water mass fraction of 80 %, heating rate of 10 K/min and feed temperature of 673 K. By applying this technology, a gaseous product was developed, named syngas, with a low carbon footprint, rich in H_2, with a calorific value comparable to other types of fossil or alternative gas fuels (Cao et al., 2019); (Bach et al., 2015).

2. BLACK LIQUOR - WASTE WITH HIGH POTENTIAL FOR ENERGY RECOVERY

Switching to greener, cleaner renewable fuel has become a mandatory target to prevent a catastrophe for nature and humanity. The pulp and paper industry uses large amounts of forest biomass, by-products or residues, including bark, forest logs. The sulphate spraying process provides 60 % of the world production of cellulose, from which it results as residual product black liquor (BL) in the amount of approximately 200 million tons. Recent research has focused on the bioconversion of BL into bio-diesel, bio-hydrogen, and bioga (Gupta and Shukla, 2019); (Rullifank et al., 2020). Natural lipids produced from the BL gasification process can be a more environmentally friendly substitute for diesel. Microbial lipids are the best alternative for biodiesel production that can be blended with diesel (from petroleum refining) in various ratios (Morya et al., 2022). H_2 yield from BL using dark fermentation can be increased by immobilizing anaerobic microbes on various matrices. However, not many studies on hydrogen production from BL have been developed due to the presence of toxic chemical compounds, as shown in Table 2. Anaerobic digestion of BL generates biogas containing 45-75 % CH_4 as the final gaseous product. The process of lowering the pH in BL makes the lignin and silica insoluble, reduces the negative impact on the environment and produces more economically attractive products (Muddassar et al., 2015). Another motivation for lignin recovery has been demonstrated in the range of 6 to 7.5 pH Losses are attributed to high pH and strong ionic strength gradients leading to lignin redissolution (Jardim et al., 2022); (Minu et al., 2012) The chemical composition of this waste from the pulp industry decides its fate for further downstream processing or upgrading (Raj et al., 2022).

Table 2. The Black Liquor Composition and properties (Wintoko et al., 2020; Anderson, 2017; Yawer et al., 2016; Whitty and Baxter 2001)

BL composition and properties	Content (%)
water	25.4
ash	53.1
C^d	30.7
H^d	4.7
O^d	37.1
S^d	5.7
Na^d	20.6
K^d	3.1
N^d	0.07
Cl^d	0.19
Ca^d	0.01
Mg^d	0.02
HHV^d (MJ/kg)	13.2
LHV (MJ/kg)	9.55
pH	11

Note: ^{d} *- dry basis, HHV = higher heat value; LHV= lower heat value*

BL is the main resource that can be further used to produce electricity, heat and biofuel. The use of energy from the gasification process allows the transformation of some modern wood processing factories into a future energy supplier, by valorizing biomass waste. BL gasification can be an alternative to pulp mill recovery boiler to produce electricity, chemicals, natural gas, H_2 or synthetic diesel. Table 3 shows the composition of the synthesis gas at the exit from the Chemrec gasifier (Naqvi and Dahlquist, 2010).

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Table 3. Wet and dry synthesis gas composition (Naqvi and Dahlquist 2010)

Parameter	Synthesis gas composition						
	CO	CO_2	H_2	H_2O	H_2S	CH_4	N_2
Temperature	*950 °C*						
Pressure	*32 bar (a)*						
Composition (% wb)	29.7	14.93	30.55	22.05	1.49	1.05	0.23
Composition (% db)	38.10	19.15	39.19	0	1.91	1.35	0.30

Note: *wb - wet basis; db - dry basis*

The BL resulting from the pulping process contains about 60 % organic substances (mainly lignin) and 40 % inorganic chemicals (mostly alkali salts) on a dry basis (Wang et al., 2015). Today, BL is burned in the Tomlinson recovery boilers to produce the steam needed to extract the pulp. Moreover the recovery boiler is also used for the retrieval of chemical products for reuse in the pulp processing process. Several studies have been done in recent years to replace recovery boilers with black liquor gasifiers (BLG) and to be integrated in pulp mills for efficient recovery of bio-based residues (Naqvi and Fröling, 2010).

3. BLACK LIQUOR GASIFICATION (BLG) PROCESS FOR THE DEVELOPMENT OF SYNGAS. TYPES OF REACTORS

Biomass gasification is an efficient and promising conversion technology. As an important novelty, CO_2-free green hydrogen production from decarbonized biomass gasification showed a promising potential to provide high energy conversion (Cormos, 2023). Gasification is a process that involves the conversion of carbonaceous materials, such as biomass, into high energy potential gases and chemicals. This process requires oxidant conditions and operating temperature of 600-1500°C (Hamaguchi et al., 2012). Gasification is widely discussed and studied to be applied in the pulp industry which helps to increase the energy efficiency of the processes and reduce the negative impact on the environment (Hruška et al., 2020). The BL gasification process is an alternative to replace classic fossil fuels, because currently this waste is only used in chemical recovery boilers in the pulp and paper industry. BL gasification offers the possibility of high thermal efficiencies, reducing production costs and creating new revenue streams through a forest biorefinery. Following the studies on the current state of gasification technologies, in relation to various projects, the type of gasifier and the used raw material, the resulting syngas capacity is presented in Table 4. Globally, the use of synthesis gas is 44%, which is produced by the installations in operation, and 27% represents the installations under development, and the remaining 29%, are planned for use.

Table 4. ***Status of gasification facilities and syngas gas capacity*** *(Shahabuddin and Tanvir 2022)*

Status	**Projects**	**Gasifiers**	**Syngas Capacity** (GWth)
Operating	379	938	173
Development	131	346	108
Planned	146	734	116
Total	656	2020	397

BLG process is conducted either using the fluidized bed reactors or fixed bed reactors. A higher air velocity is required in the case of gasification processes using fluidized/circular bed reactors compared to fixed bed reactors. The experimental reactor can be equipped with a cartridge filled with activated carbon for purifying the synthesis gas generated, respectively for the selective retention of a greenhouse gas, CO_2, thus contributing to an increase in HHV (MJ/m^3), as show in Figure 1. The

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reactor may be equipped with pressure and temperature monitoring sensors, and silica sand, used as bed material in most cases due to its good mechanical properties and inert effects. BL can be loaded in continuous flow in the preheated raw material storage area of the reactor. In addition to the reactor, the system may include: (*i*) BL storage tank, (*ii*) recirculation pump, (*iii*) dosing pump, (*iv*) flow meter and (*v*) injector (Nhut et al., 2021). Biomass gasification in fluidized bed gasifiers (FBG) is an approach for converting BL into useful gases (Yang et al., 2023). FBGs have many advantages over fixed bed gasifiers, particularly in terms of (*i*) mixing, (*ii*) reaction rates and the ability to be (*iii*) built in sizes well beyond fixed bed gasifiers (Gómez-Barea and Leckner, 2010). The fixed-bed gasification systems represent one of the most promising and efficient methods for medium-scale conversion of BL into clean heat and power (Marcel et al., 2016). Fixed bed gasifiers produce gas with a high tar or slag content depending on the processing temperature, being characterized by downward flow of coal particles under gravity. This type of gasifier involves a constant BL content supported by a grate (Asaad et al., 2022). Typically, fixed bed BL gasifiers are used to produce clean power for small-scale applications because the problems encountered contributing to gas stoppage through slag deposits leading to nozzle blockage and refractory damage (Esa et al., 2021); (Krishnamoorthy and Pisupati, 2015).

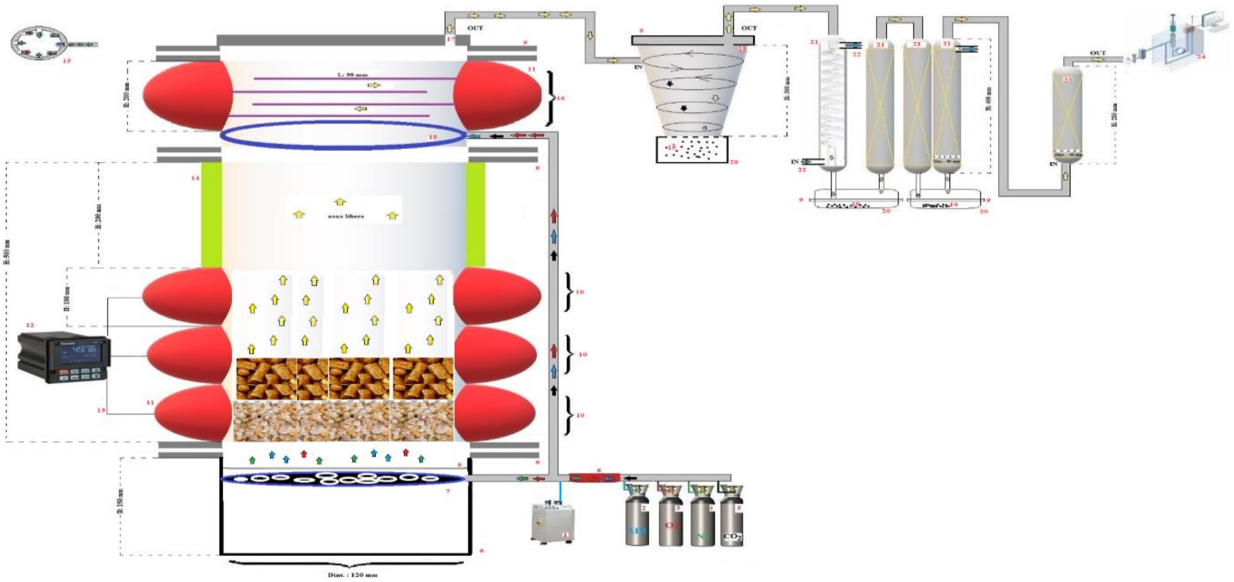

Figure 1. BL gasification process using a fluidized bed reactor

1. oxidizing agent (steam generator); 2. oxidizing agent (Air - 100 ml/min); 3. oxidizing agent (O_2; CO_2 - 100 ml/min); 4. oxidizing agent (N_2 - 100 ml/min); 5. oxidizing agent (CO_2 - 100 ml/min); 6. removable compartment of the reactor; 7. oxidizing agent nozzles (continuous flow) steel - stainless steel; 8. mesh support fluidizing bed (sand + biomass), placed over the oxidizing agent nozzle system; 9. flange; 10. fluidized bed compartment (sand/quartz + biomass) (T(°C) ambient↔1100 °C/gradient/thermal step 10°C/min); 11. heating bracelet/collar (thermocouple K, T(°C) ambient ↔ 1100°C/gradient/thermal step 10 °C); 12. PID controller T(°C) ambient↔1100 °C; 13. thermocouple K; 14. insulation (basalt wool) + sheet metal + braces; 15. oxidizing agent nozzles (continuous flow) steel - stainless steel; 16. system of sandwich steps/plates with dolomite (mesh, enough to allow gas passage, blocking ash and TAR inside the reactor to be reduced/destroyed - generates cracking reactions of Tar, resulting in CO and H_2); 17. syngas from waste biomass; 18. countercurrent cyclone (material resistant to high T(°C) of syngas; 19. fly ash and TAR; 20. fly ash collector vessel and TAR; 21. multielement/multibed condenser (syngas cooling); 22. coolant (water); 23. cartridge/BED - selective purification syngas (CO_2 retention on activated carbon bed); 24. syngas - investigation GC.

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The components of the fixed bed reactor gasifier are shown in Figure 2. Flow gasification experiments are carried out in the synthesis plant, where the syngas is cooled to - 30 °C in two stages: initially directly and later indirectly in a vertical gas cooler using BL with a high content of dry solids (Yawer, 2016). For the direct gasification of BL at - 1000 °C and an assumed 30 bar to produce a gaseous product and a liquid melt, where the product gas and the melt are separated from each other, the melt is dissolved in water forming a green liquor (Carlsson et al., 2010). The steam produced from BLG can be used either by a gas turbine or in a catalytic synthesis process to obtain fuel, it is a new technique for the production of clean electricity or new generation alternative fuels (Henrik et al., 2012).

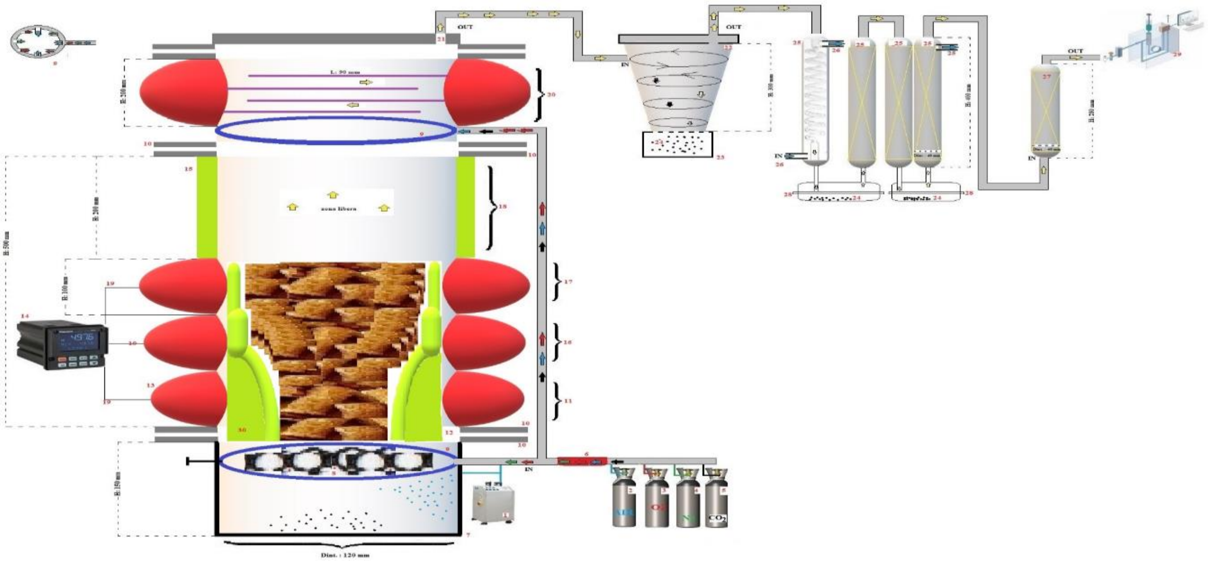

Figure 2. BL gasification process using a fixed bed reactor

1. oxidizing agent (steam generator); 2. oxidizing agent (Air - 100 ml/min); 3. oxidizing agent (O_2 - 100 ml/min); 4. agent inert atmosphere (N_2 - 100 ml/min); 5. oxidizing agent (CO_2 - 100 ml/min); 6. preheating zone (< 100 °C) of the oxidizing agent; 7. removable reactor compartment (ash collector); 8. grate (steel - stainless steel mesh, depending on the size of the granulated biomass) (actuated/rotated/shaken with semi-rings for ash removal); 9. steam nozzles (intermittent sprinkling of ash); 10. flange; 11. Reduction +oxidation/combustion compartment T(°C) ambient↔1100 °C/gradient/thermal level 10 °C/min); 12. Biomass/BL; 13. heating bracelet/collar (thermocouple K, T(°C) ambient↔1100 °C/gradient/thermal step 10 °C/min); 14. PID controller T(°C) ambient↔1100 °C;15. insulation (basalt wool) + sheet metal + braces; 16. devolatilization/pyrolysis compartment (T(°C) ambient↔50 0 °C/gradient/thermal ramp 10 °C/min); 17. drying compartment T(°C) ambient↔105 °C/gradient/thermal level 10 °C/min); 18. free zone compartment (ambient T(°C); 19. thermocouple K; 20. system of sandwich steps/plates with dolomite (mesh, enough to allow gas passage, blocking ash and TAR inside the reactor to be reduced/destroyed - generates cracking reactions of Tar, resulting in CO and H_2); 21. syngas - from waste biomass/BL; 22. countercurrent cyclone (material resistant to high T(°C) of syngas; 23. fly ash and TAR collector vessel; 24. fly ash and TAR; 25. multielement/multibed condenser (syngas cooling);26. coolant (water); 27. cartridge/BED - selective purification syngas (CO_2 retention on activated carbon bed); 28. flange - collector vessel; 29. syngas - investigation GC; 30. movable convex fins.

BL, which is composed of - 30 % moisture, 35 %, inorganic chemical compounds and 35 % combustible material (Carlsson et al., 2008), subjected to the gasification process, goes through the following stages: (i) drying-partial release stage the content of water raw materials, (ii) decomposition into coal, tar, oil, gas and other gasification products, (iii) oxidation in air, CO_2 mixed with the steam atmosphere. (Jafarikojour et al., 2014); (Serres et al., 2018); (Wojewódka et al., 2019). The gasifier is designed to carry out the process of burning the fuel. Basically, it starts from the drying chamber and automatically feeds itself during stable operation. The heat from combustion removes moisture from the BL as well as other particles from the pyrolysis zone. However, it is important to note that the temperature must reach > 800 °C in the reactor to produce gas (Hoque and Rashid, 2021). Pressure gasification of BL at high temperature is a potential complement to the recovery boiler traditionally used to recover chemicals and energy from the BL in the Kraft pulping process. In all cases, the gasification plant at the pulp mills has a shortage of steam, also having a low pressure, therefore the mill supplies steam at medium pressure to the gasification plant, while the excess of steam at low pressure is returned to the processes of manufacture of cellulose (Andersson et al., 2016). This steam from the gasification process has many uses in pulp and paper mills especially for papermaking machines or fresh water deaerators, as well as in the desorption column. (Hruška et al., 2020). Cold gas efficiency is defined as the ratio of the energy flow from the gas to the energy contained in the BL. Increasing the steam-to-fuel ratio generally leads to increased production of CO, H_2, CO_2, CH_4. By adding more steam, the amount of CO decreases, which decreases the efficiency of the cold gas. In order to maintain the temperature at 1000 °C during gasification, a higher steam-to-fuel ratio (ER) is required, which means that more air should be supplied to provide more heat in the reactor by burning the carbon (Arif et al., 2018). At reduced reactor load, having a low BL flow rate, wall heat losses will play a greater role in the thermal balance of the reactor. Therefore, in order to keep the temperature constant at low reactor load, the oxygen to BL ER must be increased. Consequently, at low BL flow rates, the CO_2 content of the gas will increase as more CO, CH_4 and H_2 will be burned to CO_2 and H_2O. Also, the increase in CO and H_2 can be related to the decrease in oxygen from the BL gasification process (Carlsson et al., 2010); (Wiinikka et al., 2012). The main components of the syngas resulting from BL following the gasification process are H_2, CO and CO_2 and smaller amounts of H_2S, CH_4 and heavy metals. Therefore, the initial levels of metals, from BL, most likely migrated to the solid residue (Serres et al., 2016); (Akpoveta and Osakwe, 2014).

4. MARKET OPPORTUNITIES FOR BLG

In terms of economic valorization, BL can be transformed into several valuable compounds, methanol, succinic acid, and gases, H_2, CH_4, demonstrating its value as a powerful resource, such strategies contributing to the reduction of the environmental degradation (Raj et al., 2022). The results of additional studies conducted to elaborate and understand the economic feasibility, encourages the research for further economic evaluation, especially for the development of a real valuable product or commercial application (Andrew et al., 2014). The technology of BL gasification promises to be widely accepted. The use of coal in conventional combustion technology has been stopped worldwide. Therefore, gasification technology could be the crucial alternative in using this cheap and reliable energy resource in the foreseeable future. The best BLG solution in Europe is the Chemrec R&D plan, the Chemrec BLG system currently uses the most advanced pressurized oxygen driven flow gasifier and can produce synthesis gas at a high temperature, separating the inorganics from the black liquor in the section of extinguishing the gasifier (Naqvi et al., 2012). The biorefinery aims to produce cellulose and use BLG syngas to produce dimethyl ether (DME) fuel which is clean burning and brings much greater advantages over diesel. This dimethyl ether fuel kept the economic projections active due to the revenue brought by this DME compound (Mongkhonsiri et al., 2021); (Bajpai, 2014). The results show that BL gasification is an attractive technology to generate electricity co-generated energy based on gas turbines (Eriksson and Harvey, 2004). Liquid and gaseous products

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from BL gasification could be an interesting route for obtaining fuel gases and value-added bioproducts (Barros et al., 2022).

5. CONCLUSIONS

By applying the BL gasification processing technology, the following effects will be obtained: (*i*) limiting GHG (greenhouse gases) emissions CO_2, CH_4, N_2O, generated by specific activities; (*ii*) balancing energy consumption through *in situ* development of biofuels through thermochemical gasification processes. Modern pulp mills can contribute to the supply of fuel and natural gas from the recovery of waste, thereby reducing dependence on fossil resources. The syngas obtained from the BL gasification processes is more efficient compared to fossil fuels. Among the different methods of energy production (pyrolysis, gasification, incineration), the gasification process is the most suitable, because it takes place in the presence of oxygen and generates a more valuable final product from an energetic point of view. Modern pulp mills can help provide fuel and natural gas from waste recovery, thereby reducing dependence on fossil resources. I can implement both fixed-bed reactor models, which are the most advantageous because they have medium-scale BL conversion methods, but also fluidized-bed ones, where a higher speed of the oxidizing agent is required in the gasification process that uses reactors with fluidized/circular bed compared to fixed bed reactors. BL capitalization strategies demonstrate for the generation of value-added products. Products generated from the gasification process will contribute to the reduction of environmental degradation caused by the waste from the kraft processes, the black liquor. The transformation of this waste waste into valuable resources is a key pathway for the sustainability of lignocellulosic industries. Black liquor, as I mentioned earlier, is a source with a high carbon potential that has demonstrated that through various methods it can produce products such as polyhydroxyalkanoate, biodiesel, biohydrogen, biogas, etc.

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