

ANALYSIS OF COGENERATION SYSTEMS WITH GASIFICATION OF BLACK LIQUOR IN THE PAPER AND CELLULOSE SECTOR

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Abstract. *The pulp and paper sector is intensive in the use of energy, and presents a high participation in the industrial context, specially based in renewable source generated in the pulp process. Although the black liquor gasification (BLG) is not still completely dominated, it has the potential of becoming an important alternative for the pulp and paper sector, once the burning of BLG in gas turbines should guarantee higher efficiencies, better use of the available renewable resources, also allowing the chemical recovery, just as is done nowadays with Tomlinson chemical recovery steam generators. In this article, it will be developed an analysis of the pulp and paper sector identifying its energy and environmental participation in the context of the national matrix. Based on the Rankine cycle, taken as the current state of knowledge, an energetic and exergetic analysis of a cogeneration system based on BLG system associated to gas turbine, heat recovery steam generator and backpressure steam turbine with extractions will be developed. The proposed scheme will be developed to produce electric/mechanical power and two pressure steam for guaranteeing better operational conditions comparatively to the traditional system.*

Keywords: *Cogeneration, black liquor, gasification*

1. INTRODUCTION

Currently, the pressing concern related to the environment and reduction of fossil fuels has led researchers to focus on new technologies for the energy conversion for minimizing the impacts on nature and warranting the human survival on Earth. Renewable energy sources may be a solution to the offering of alternative energy because the greenhouse effect and global climate change are minimized.

There are several renewable energy sources to be considered, and Brazil stands out for having environmentally-friendly resources in abundance, such as hydropower, biomass, solar and wind. However, the water resources are already being affected by climate change, which means that rain dynamics is changing. Vegetal and agricultural biomasses are a source of energy obtained from the sun, a renewable and inexhaustible source in the long term, through the natural photosynthesis process. The use of this fuel is enabled to have a neutral CO₂ emission balance and also there is a great absorption of this gas by the biomes. The great advantage for Nature is the reduction of greenhouse effect, as a consequence of CO₂ emissions decrease.

Biomass is available in so many ways, as in the large surpluses of timber forests, agricultural waste and organic fractions of municipal solid wastes. The importance of energy obtained from biomass is dependant of its availability in natura; the conversion of solid biomass to gas is also important to be proposed because some more efficient additional technologies (other than steam thermal power plants, based on steam generators and incinerators), such as gas turbines, can be employed.

Biomass is easier to gasify than fossil fuels because biomass contains its oxygen and water in its chemical structure, crucial elements in the gasification process. The gasification allows the conversion of solid material into combustible gases, generating energy to be processed to mechanical and/or electrical energy, as well as the production of synthetic fuels and chemicals.

In this paper, an energetic and exergetic analysis of a black liquor-integrated gasification combined cycle is presented. Based on the integrated gasification combined cycle scheme proposed by Larson *et al.* (2000), a black liquor and a green liquor compositions were established, according to the literature; mass, energetic and exergetic balance equations were then applied to each component and the available data were considered for validating the analysis. Gas turbine energetic and exergetic analysis are presented in details, and data relative to the energetic and exergetic analysis of black liquor-integrated gasification combined cycle scheme is then presented.

2. GAS TURBINE - ENERGETIC AND EXERGETIC ANALYSIS

The thermodynamic analysis of a gas turbine is based on the scheme proposed in Fig. 1. Table 1 registers the physical properties of points relative to inflows and outflows; Table 2 presents the composition of synthesis gas that is burnt in the gas turbine's combustion chamber, as the result of chemical equilibrium calculations (Gordon and McBride, 1971); the black liquor composition (Consonni *et al.*, 1998) was due to Phyllis (2007).

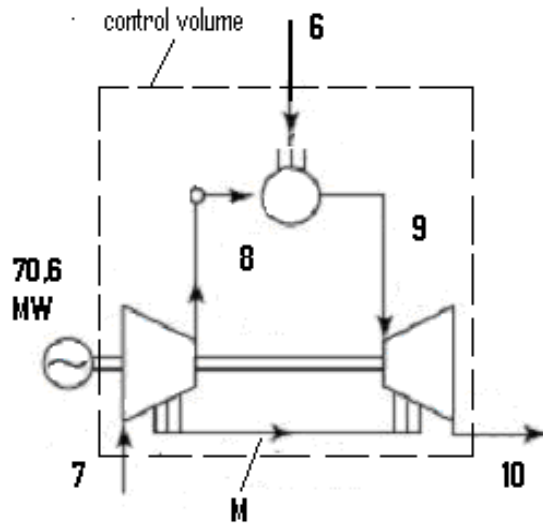


Figure 1 – Gas turbine

Table 1 - Properties of the entrances and exits of the gas turbine

	Description	$\dot{m}(kg / s)$	$T(^{\circ}C)$	P (MPa)
6	entrance of fuel	62.3	130	2.31
7	entrance of air ($15^{\circ}C$)	190	15	0.101
8	entrance of air ($423^{\circ}C$)	105	423	1.71
9	combustion gas exit	167.3	1280	1.66
10	exhaust gas exit	202	585	0.104

Table 2 - Composition of the synthesis gas in the gasifier exit

Composition of the gas	n_{i1}	n_{i2}	%vol _{i1}
H ₂	0.1549	0.155305	15.53
H ₂ O	0.088793	0.088985	8.90
H ₂ S	0.0025588	-	-
NH ₃	0.0000074359	-	-
CO	0.1909	0.191399	19.14
COS	0.00010092	-	-
CO ₂	0.07531	0.075507	7.55
N ₂	0.4875	0.488774	48.88
Total	1.0230993559	0.999935	100.00

Based on the synthesis gas composition, the exhaust gas composition at the combustion chamber exit is modeled according to the Eq. (1). Considering a reasonable 10% air excess in the combustion process, the exhaust gas composition is presented in Tab. 3.

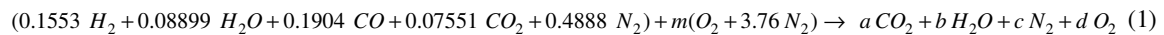


Table 3 - Composition of the gas that leaves the combustion chamber

Composition of the gas	n_{i3}	%vol _{i2}
CO ₂	0.26691	15.3900
H ₂ O	0.24429	14.0857
N ₂	1.205776	69.5248
O ₂	0.017335	0.9995
Total	1.734311	100.0000

2.1 Energetic analysis of the gas turbine

The specific heat of the exhaust gas (c_{p_g}) was calculated according to the Tab. 3 data; the specific heat equations for carbon dioxide, water (steam), nitrogen and oxygen were used (Perry and Green, 1999; Dias and Balestieri, 2003); in this way, an expression to characterize the variation of the specific heat of the exhaust gas in the gas turbine as a function of its temperature was elaborated Eq. (2).

$$c_{p_g}(T) = \frac{0.1539}{44} \bar{c}_{pCO_2} + \frac{0.140857}{18} \bar{c}_{pH_2O} + \frac{0.695248}{28} \bar{c}_{pN_2} + \frac{0.009995}{32} \bar{c}_{pO_2} \quad (2)$$

In Equation (2), the numerator expresses the product of the molar fractions of each chemical substance multiplied by its characteristic specific heat in molar base, and the denominator refers to the molecular weight. They are considered the specific heats of CO₂, H₂O, N₂ and O₂ respectively:

$$c_{p_g}(T) = \frac{0.1539}{44} (10.34 + 0.00274 \cdot T - \frac{195500}{T^2}) + \frac{0.140857}{18} (8.22 + 0.00015 \cdot T + 0.00000134 \cdot T^2) + \\ + \frac{0.695248}{28} (6.5 + 0.001 \cdot T) + \frac{0.009995}{32} (8.27 + 0.000258 \cdot T - \frac{187700}{T^2})$$

This complete expression is then reduced and converted to the International System to generate Eq. (3).

$$c_{p_g}(T) = 1.107288 + 0.000149T + 4.39029 \cdot 10^{-8} T^2 - \frac{3108.42}{T^2} \left(\frac{kJ}{kg \cdot K} \right) \quad (3)$$

For the exhaust gas temperature obtained in the Tab. 1, T=585°C=858 K, $c_{pg}(T=858 \text{ K}) = 1.263516 \text{ (kJ/kgK)}$.

The specific heat of the air ($c_{p_{ar}}$) is calculated by the equation proposed by Shieh and Fan (1982) for the air compressor entrance temperature, of T=15°C=298 K, according to Tab. 1:

$$c_{p_{ar}}(T) = 1.04841 - 0.00038372T + \frac{9.45378}{10^7} T^2 - \frac{5.49031}{10^{10}} T^3 + \frac{7.92981}{10^{14}} T^4 \quad (4)$$

$$c_{p_{ar}}(T = 298 \text{ K}) = 1.00374 \text{ kJ / kgK}$$

As there is no information about the percentage of compressor entrance air is used for its refrigeration, an estimate is done considering that ($\dot{m}_M$) 34.3 kg/s of ($\dot{m}_{ar}$) 190 kg/s entrance air is sent to the gas turbine via the M point of Fig.

1. As the net gas turbine power ($\dot{W}_{liq}$) is of 70,600 kW, the temperature of air injection (T_M) can be estimated by Eq. (5). The mechanical efficiency (η_m) of gas turbine is 93.5%.

$$\dot{W}_{liq} = \dot{m}_g \cdot c_{p_g} \cdot (T_9 - T_{10}) - \frac{1}{\eta_m} \cdot c_{p_{ar}} \cdot [\dot{m}_{ar} \cdot (T_8 - T_7) + \dot{m}_M \cdot (T_M - T_7)] \quad (5)$$

$$70600 = 167.3 \cdot 1.263516 \cdot (1280 - 585) - \frac{1}{0.935} \cdot 1.00374 \cdot [155.7 \cdot (423 - 15) + 34.3 \cdot (T_M - 15)]$$

Therefore, $T_M = 235.45^\circ\text{C}$

For the available data, the compressor isentropic efficiency (η_{cp}) (Bathie, 1984; Boyce, 2002; Cohen and Saravanamuttoo, 1987) can be calculated for the data of Tab. 1. In the compressor, admitting k=1.4 for the air, $T_8=423^\circ\text{C}$, $T_7=15^\circ\text{C}$, $P_8=1.7 \text{ MPa}$ and $P_7=10 \text{ kPa}$, the values are calculated by using Eq. (6).

$$\frac{T_8}{T_7} = \left\{ 1 + \frac{1}{\eta_{cp}} \left[\left(\frac{P_8}{P_7} \right)^{\frac{k-1}{k}} - 1 \right] \right\} \quad (6)$$

$$r = \frac{P_8}{P_7} = \frac{17.1}{1.01} = 16.93 \quad \text{and} \quad \frac{423+273}{15+273} = \left\{ 1 + \frac{1}{\eta_{cp}} \left[(16.93)^{\frac{0.4}{1.4}} - 1 \right] \right\} \Rightarrow \eta_{cp} = 0.8782$$

For the temperature of the point M (T_M), the pressure ratio (r) will be:

$$r = \frac{P_M}{P_7} = \left(\frac{T_M}{T_7} \right)^{\frac{k}{k-1}}, \text{ therefore corresponds to } r = \left(\frac{235.45+273}{15+273} \right)^{\frac{1.4}{1.4-1}} \Rightarrow r = 7.3113$$

The thermal efficiency of the gas turbine, based on the 1st Law of Thermodynamics (η_I) is given by Eq. (7).

$$\eta_I = \frac{\dot{W}_{lig}}{\dot{m}_{comb} \cdot PCI} \quad (7)$$

for which $\dot{m}_{comb} = 62.3 \text{ kg/s}$ is the flow of clean synthesis gas that enters in the combustion chamber and $PCI = 3,780 \text{ kJ/kg}$ is the clean synthesis gas lower heating value (PCI).

$$\eta_I = \frac{70600}{62.3 \cdot 3780} \Rightarrow \eta_I = 0.2998$$

2.2 Exergetic analysis of the gas turbine

The exergetic analysis of gas turbine system is described below according to the flow numbers described in Fig.1.

a) Exergy of the entrance air (ex_{ar}) in the compressor (flow 7) (Kotas, 1985)

$$ex_{ar} = c_{p_{ar}} [(T - T_0) - T_0 \ln \frac{T}{T_0} + \left(\frac{\gamma-1}{\gamma} \right) T_0 \ln \frac{P}{P_0}] \quad (8)$$

From the Table 1 it is obtained the data for the air; polytropic index is assumed to be $\gamma = 1.4$. Reference state is given for temperature $T_0 = 298 \text{ K}$ and pressure $P_0 = 101 \text{ kPa}$. The specific heat of the air for the temperature of entrance of the air in the entrance of the compressor $T = 15^\circ \text{C} = 288 \text{ K}$ was previously calculated and its value is $c_{p_{ar}} (T = 298 \text{ K}) = 1.00374 \text{ kJ / kgK}$.

In this way, the specific exergy of entrance air (ex_{ar}) is:

$$ex_{ar} = 1.00374 [(288 - 298) - 298 \ln \frac{288}{298} + \left(\frac{1.4-1}{1.4} \right) 298 \ln \frac{101}{101}] \Rightarrow ex_{ar} = 0.1723 \text{ kJ / kg}$$

and consequently the exergy of the air ($\dot{Ex}_6$), for the mass flow obtained from Tab. 1 is finally calculated.

$$\dot{Ex}_6 = \dot{m}_{ar} \cdot ex_{ar} = 190 \cdot 0.1723 = 32.73 \text{ kW}$$

b) Exergy of clean synthesis gas that enters in the combustion chamber (flow 6)

The exergy of clean synthesis gas is calculated for the combustion chamber entrance temperature, at $T = 130^\circ \text{C} = 403 \text{ K}$, according to Tab. 1; it is calculated according to physical and chemical components (Balestieri, 2002) represented by Eq. (9) and Eq. (10). The corresponding values are obtained of the Tab. 4.

- Physical exergy:

$$ex_g^F = \sum_{i=p} a_i \{ \bar{h}(T) - \bar{h}(T_0) - T_0 [\bar{s}(T) - \bar{s}(T_0) - \bar{R} \ln \frac{x_i \cdot P}{P_{00}}] \} \quad (9)$$

with a_i coefficient for balancing the equation of combustion;

$\bar{h}$ enthalpy at the base molar;

$\bar{s}$ entropy at the base molar;

x_i mole fraction of each component of the equation of combustion;

$\bar{R} = 8.3144 \text{ kJ/kmol}$, $P = 2.31 \text{ MPa}$, $T = 403 \text{ K}$, $P_{00} = 101 \text{ kPa}$ and $T_0 = 298 \text{ K}$.

- Chemistry exergy:

$$ex_g^Q = \sum x_i \bar{e}_i^Q + \bar{R} T_0 \sum x_i \ln x_i \quad (10)$$

Table 4 – Thermodynamic properties of clean synthesis gas that enters in the combustion chamber, referred to Tab. 2.

	CO	CO ₂	H ₂	N ₂	H ₂ O
a_i	0.191399	0.075507	0.155305	0.488774	0.088985
x_i	0.1914	0.0755	0.1553	0.4888	0.089
$\bar{h}$ (kJ/kmol) T(403K)	11732.2	13495.5	11513.6	11727.6	13458.9
$\bar{h}$ (kJ/kmol) T ₀	8669	9364	0	8669	9904
$\bar{s}$ (kJ/kmolK) T(403K)	206.3425	225.5325	139.32	200.29	198.93
$\bar{s}$ (kJ/kmolK) T ₀	197.54	213.69	130.57	191.50	188.72
$\bar{e}^Q$ (kJ/kmolK)	269419	14175	235250	640	8635

Specific physical and chemical exergy components are calculated below, according to Eq. (9) and Eq. (10).

$$ex_g^F = 6143.67 \text{ kJ/kmol}$$

$$ex_g^Q = 86868.31 \text{ kJ/kmol}$$

The molecular weight of the clean synthesis gas (M_g) is then calculated, and its value is used for estimating physical and chemical exergy components of synthesis gas.

$$M_g = \sum x_i \cdot M_i = 0.1914 \cdot 28 + 0.0755 \cdot 44 + 0.1553 \cdot 2 + 0.4888 \cdot 28 + 0.089 \cdot 18 = 24.2802 \text{ (kg/kmol)}$$

$$\dot{n}_g = \frac{\dot{m}_g}{M_g} = \frac{62.3(\text{kg/s})}{24.2802(\text{kg/kmol})} = 2.566 \left(\frac{\text{kmol}}{\text{s}} \right)$$

$$\dot{Ex}_g^F = 6142.67 \cdot 2.566 = 15764 \text{ kW}$$

$$\dot{Ex}_g^Q = 86868.31 \cdot 2.566 = 222893 \text{ kW}$$

whose clean synthesis gas total exergy ($\dot{Ex}_s$) is:

$$\dot{Ex}_s = 238657 \text{ kW}$$

c) Exergy of the gas that leaves the gas turbine (flow 10)

The exergy of gas turbine exhaust gas is calculated for thermodynamic properties collected of the Tab. 3 and by using Eq. (9) and Eq. (10): $P=104\text{ kPa}$, $T=858\text{ K}$, $P_{00}=101\text{ kPa}$ and $T_0=298\text{ K}$. With the data of the Table 5, the physical exergy and the chemical exergy of the exhaust gas are calculated from the gas turbine.

Table 5 - Properties of the exhaust gas of the gas turbine, referred to Tab. 3.

	CO	H ₂ O	N ₂	O ₂
a_i	0.26691	0.24429	1.20578	0.01734
x_i	0.1539	0.1409	0.6952	0.01
$\bar{h}$ (kJ/kmol) T(858K)	35191.4	30161.2	25546.4	26490.8
$\bar{h}$ (kJ/kmol) T ₀	9364	9904	8669	8682
$\bar{s}$ (kJ/kmolK) T(858K)	261.04	226.43	223.12	238.184
$\bar{s}$ (kJ/kmolK) T ₀	213.69	188.72	191.50	205.033
$\bar{e}^Q$ (kJ/kmol)	14175	8635	640	3950

$$ex_g^F = 10874.97 \text{ kJ / kmol}$$

$$ex_g^Q = 1744.55 \text{ kJ / kmol}$$

The molecular weight of the exhaust gas (M_g) is then calculated, and its value is used for estimating physical and chemical exergy components of exhaust gas.

$$M_g = \sum x_i \cdot M_i = 0.1539 \cdot 44 + 0.1409 \cdot 18 + 0.6952 \cdot 28 + 0.01 \cdot 32 = 29.0934 (\text{kg / kmol})$$

$$\dot{n}_g = \frac{\dot{m}_g}{M_g} = \frac{202 (\text{kg / s})}{29.0934 (\text{kg / kmol})} = 6.943 \frac{\text{kmol}}{\text{s}}$$

$$\dot{Ex}_g^F = 10874.97 \cdot 6.943 = 75506 \text{ kW}$$

$$\dot{Ex}_g^Q = 1744.55 \cdot 6.943 = 12113 \text{ kW}$$

In this way, the exhaust gas total exergy is:

$$\dot{Ex}_{10} = 87619 \text{ kW}$$

2.3 Exergetic irreversibility and efficiency of the gas turbine

The calculation of the irreversibility ($\dot{E}_d$) (Moran and Shapiro, 2002) of the gas turbine is obtained by using Eq. (11).

$$0 = \sum_e \dot{m} \cdot ex_e - \sum_s \dot{m} \cdot ex_s - \dot{E}_d \quad (11)$$

Therefore, the irreversibility ($\dot{E}_d$) of the gas turbine will be:

$$\dot{E}_d = 238690 - 158219 = 80471 \text{ kW}$$

The exergetic efficiency (η_{II}) (Kotas, 1985) can be defined by Eq. (12):

$$\eta_{II} = \frac{\sum \dot{E}x_s}{\sum \dot{E}x_e} \quad (12)$$

Therefore the efficiency of the 2nd law of Thermodynamics (η_{II}) for the gas turbine will be:

$$\eta_{II} = \frac{\dot{E}x_{10} + \dot{W}_{liq}}{\dot{E}x_8 + \dot{E}x_6} \Rightarrow \eta_{II} = \frac{87619 + 70600}{238657 + 32.73} \Rightarrow \eta_{II} = 0.6628$$

3. INTEGRATED GASIFICATION COMBINED CYCLE EXERGETIC ANALYSIS

The complete cogeneration scheme considered in this analysis is an air-blown black liquor integrated gasification combined cycle that is presented in Fig. 2. The results of exergetic efficiency and irreversibility for the main components are presented in Tab. 6.

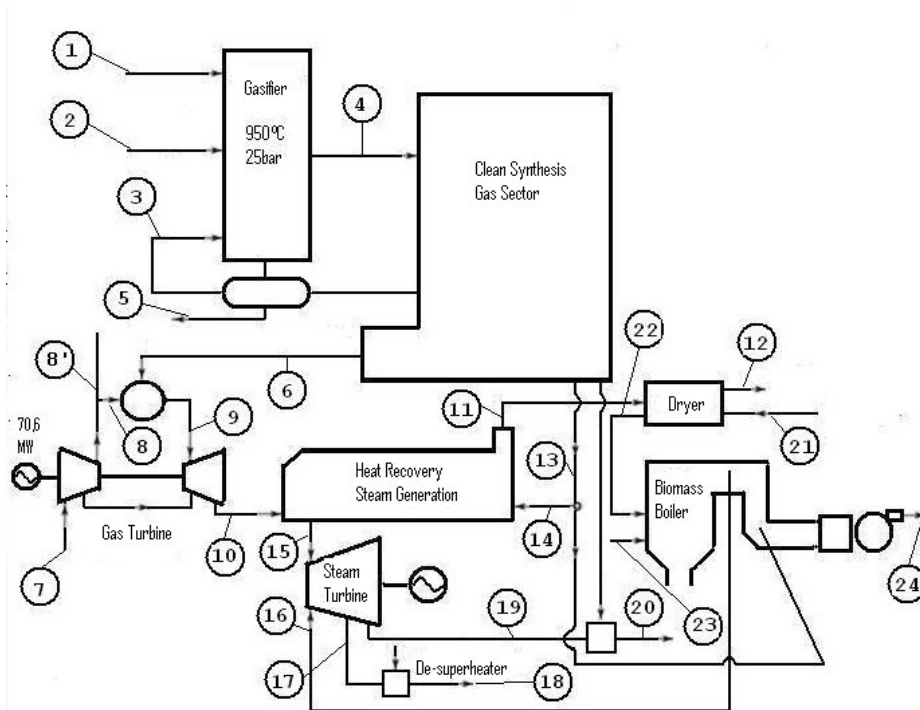


Figure 2 – Basic scheme of air-blown black liquor integrated gasification combined cycle

Table 6 – Exergetic efficiency and irreversibility for the scheme proposed in Fig. 2

Description of components	η_{II} (%)	$\dot{E}_d$ (kW)
gasifier	48.05	521093
gas turbine	66.28	80471
heat recovery steam generation	48.45	46404
steam turbine	96.71	3116

The above results do not exactly match the ones obtained by Gallego (2004), except for the gasifier, whose gasifier second law efficiency was 53%. However, it must be noted that several differences are present: Larson *et al.* (2000) and Gallego (2004) taken specific black liquor composition that is different from the one here considered; some other thermodynamic properties differ, such as component efficiencies, and this is decisive for the results obtained.

4. CONCLUSIONS

The analysis of an air-blown black liquor integrated gasification combined cycle here described was developed considering the scheme proposed by Larson *et al.* (2000); however, as the authors do not present the formulation used to develop their calculation, and also some important parameters are missing, it was structured a sequence of calculations to reproduce the modeling of such cogeneration unit.

Some of the obtained values were not completely reproduced, when compared to the ones presented in the above reference, because the black and green liquor compositions had to be adopted; however, the modeling was validated and is presenting adequate values of energetic and exergetic analysis.

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