Exergy Analysis of Cryogenic Air Separation Unit Integrated with Biomass Gasifier

S.N. Sapali, V. N. Raibhole

Abstract— **Cryogenic air separation is the main method to separate air into its constituents like oxygen, nitrogen and argon. Medium purity cryogenic air separation units are mostly required for gasification. As air gasification produces poor quality syngas, oxygen is used as gasifying agent for biomass gasification. Biomass gasification with oxygen as gasifying agent has great potential in applications like integrated gasification combined cycle (IGCC), chemical production and Fischer-Tropsch (F-T) processes. Cryogenic air separation is the process of high energy consumption. In this work, the simulation of medium purity cryogenic air separation integrated with biomass gasifier is performed by using Aspen plus. Exergy analysis of cryogenic air separation and gasification process is performed to check the thermodynamic perfection of the process. It is found that cryogenic ASU produces oxygen with purity 96.2 %mole basis with specific power consumption 0.2435 kW/scmh of O_2. The parameters like syngas composition and heating value also predicted in simulation of biomass gasifier. The exergy loss and exergetic efficiencies of unit operations are also calculated on the basis of simulation results. It is observed that major exergy loss is taking place in main heat exchanger, compressor and distillation units.**

Index Terms— **ASU, ASPEN plus, Exergy, IGCC, Syngas**

I. INTRODUCTION

The industrial gases like oxygen, nitrogen and argon are produced in gaseous or in liquid form in a wide variety of purities by separating air using a cryogenic technology. The development of cryogenic air separation unit (ASU) has been taken place through various stages. As the process cycle improvement is one of the areas for further development in cycle towards performance, it is essential to understand thermodynamics of the process cycle, simulation of various unit operations in a cryogenic ASU. ASPEN plus is one of the process simulator used for modeling cryogenic air separation plant and biomass gasification. It is a steady state chemical process simulator. It uses unit operation blocks, which are models of specific process operations (reactors, heaters, pumps etc.). The user places these blocks on a flow sheet, specifying material and energy streams.

The continuous development of air separation cycles has been taking place in terms of recovery, power consumption, purity, cost of manufacturing, ease of maintenance etc [1-8]. As cryogenic air separation is the energy intensive process for which exergy analysis and energy integration are useful tools. The exergy analysis of cryogenic air separation plant was performed and exergy loss calculated for different sections of the plant in [9-10]. Efficient cryogenic ASU integrated with gasification process for supplying oxygen with required purity. Gasification involves the production of gaseous fuel mainly consisting of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and with traces of methane (CH_4); with useable heating value by partial combustion of solid fuel. Feedstock's of gasification like biomass and inferior quality coal have great potential for energy production. Currently energy is recovered from these fuels through combustion. The efficiency of these plants is very less. Thus coal/biomass gasification unit integrated with combined power cycle offers higher efficiencies up to 60% [11]. As one of the attempt to study performance of gasifier with air as gasifying agent, an equilibrium model based on minimization of Gibbs free energy was developed for rubber wood and syngas composition obtained [12], whereas mathematical model in Engineering Equation Solver (EES), was used to predict syngas composition in a small downdraft gasifier [13]. However thermodynamic equilibrium composition prediction is the important step in modeling the gasification process. An equilibrium model for biomass gasifier was developed and equilibrium relations were solved by using MATLAB to get syngas composition and its properties [14]. In addition to this exergy analysis performed on the basis of thermodynamic equilibrium for different feed stocks [15-16]. In today's scenario biomass gasification with oxygen as gasifying agent has great potential for various applications.

The aim of the present work is to simulate medium purity oxygen cryogenic plant by using Aspen plus for gasification application and found out specific power consumption. It is also an attempt to develop a model of biomass/coal gasifier with oxygen and steam as oxidizing agent by using Aspen plus. Simulation of biomass gasifier based on Gibbs free energy minimization is performed. The syngas is obtained with various parameters like syngas composition, temperature, heating value for different feed stocks as rice husk, wood pallets and Indian charcoal. In addition to this exergy analysis of cryogenic ASU and biomass gasifier is also performed.

II. Simulation of Cryogenic ASU for Gaseous Oxygen Production

The cryogenic distillation of air is currently the only method available for the large oxygen production rates required for future fossil fuel gasification and oxy-fuel combustion with CO_2 capture. The current large scale users

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S. N. Sapali is Professor and Head, Department of Mechanical Engineering, with the College of Engineering, Pune-411005 Maharashtra, India. phone: 020-25507224; Mobile: +91 9423582575;
(e-mail: k_sapali@yahoo.co.in)
V. N. Raibhole is Associate Professor, Department of Mechanical Engineering. with MES's College of Engineering, Pune-411001, Maharashtra, India; (e-mail: vraibhole@gmail.com)

are the chemical, steel and petroleum industries. O_2 purities of up to 97% are favored for gasification application as this requires the much easier separation of N_2 from O_2. Production of 99.5% O_2 requires the more difficult O_2/Ar separation with up to double the number of separation stages in a distillation column. A process flow sheet for the cryogenic air separation system is shown in Part-I of Fig.1. Separation of over 95% of the O_2 in the air feed at 90% to 97% molar concentration is carried out in two distillation column thermally linked by a dual-function heat exchanger called as reboiler/condenser. This heat exchanger serves as a reboiler for the high pressure column (HP) and as a condenser for low pressure column (LP). The LP column operates at low pressure 1.2 bar which are close to ambient pressure to minimize energy use. The HP column operates at pressure 4 bar.

Filtered air is first compressed to 4.2 bar and cooled to 45^0C temperature by water cooled heat exchanger. The compressed air then enters a main heat exchanger and is further cooled and partially liquefied by countercurrent heat exchanger with cold nitrogen and oxygen streams from the columns. Partially liquefied air at 4.2 bar pressure enters the high pressure column. The separated N_2 gas condenses to provide reflux to the HP column and enters to the LP column after sub cooling in the sub-cooler. Up to 30% of the air is further compressed to a pressure of 50 bar which gives a positive temperature difference. The refrigeration balance on the plant is provided by expanding a portion of the high pressure air stream in a turbine. The discharge air stream from expander is feed to LP column. The O_2 rich liquid stream and a high pressure fraction of the air which has been liquefied are the feed streams to the LP column. The distillation separates an N_2 gas stream from top of LP column and a liquid O_2 stream from bottom of LP column are supplied to main heat exchanger and heated to ambient temperature, which cools and partially liquefies the air feed streams.

The simulation model of biomass gasification consists of two stages as biomass decomposition and gasification reaction with steam and oxygen. In decomposition, biomass is decomposed into its elements like C, H, O, S, N and H_2O.The Aspen plus yield reactor DECOMP is used to simulate decomposition of the feed. The stream Biomass is specified as non-conventional stream and ultimate and proximate analysis are given as input along with thermodynamic condition and mass flow rate. The Aspen plus Gibbs reactor GASFR is used for partial combustion based on assumption that reactions of biomass elements with oxygen follow Gibbs equilibrium. The Process flow diagram of biomass gasification with oxygen and steam is shown in part-II of Fig.1. The simulation parameters for cryogenic ASU integrated with biomass gasifier are given in Table I.

TABLE I

SIMULATION PARAMETERS FOR CRYOGENIC ASU INTEGRATED WITH BIOMASS GASIFIER

Parameter	Quantity
Air flow	1000 scmh
Compressor discharge pressure	4.2 bar
LP Pressure	1.2 bar
HP Pressure	4 bar
No. of stages in LP column	56
No. of stages in HP column	40
Heat leak	15 kW
Oxygen flow rate	10.0 kg/hr,
Steam flow rate	8 kg/hr
Input biomass mass flow	33.6 kg/hr
Gasification pressure	1.05 bar

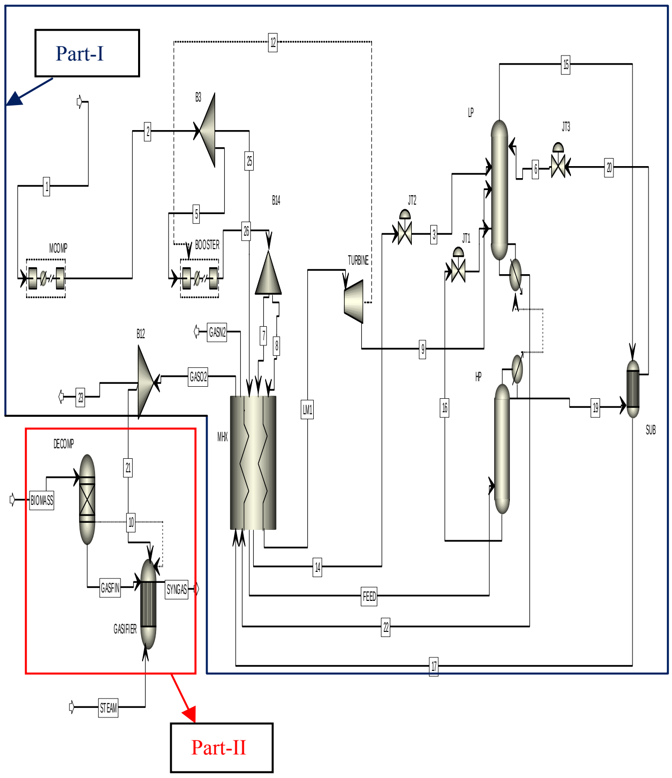

Fig 1. Process flow diagram of cryogenic ASU integrated with biomass gasifier

III. Exergy

Exergy is the quantity of work, which can be extracted by an external energy consumer during a reversible interaction between a system and surrounding until the complete equilibrium is reached. The total exergy transfer rate of a material stream can be calculated with following expression.

$$\dot{E} = \dot{E}_k + \dot{E}_p + \dot{E}_{phy} + \dot{E}_{Chem} \tag{1}$$

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Where:

$E_k = m\left(\frac{C_0}{2}\right)$ Represents the kinetic exergy rate, where C_0 is the speed of stream flow relative to earth surface

$E_p = \dot{m} g Z_0$ Represents the potential exergy rate, where g is the earth gravity and Z_0 is the stream altitude above the sea level

$\dot{E}_{phy}$ Represents the thermo mechanical exergy based on temperature and pressure of stream

$\dot{E}_{Chem}$ Represents the chemical exergy based on chemical potential of components in the stream

The specific exergy can be written as:

$$e = e_k + e_p + e_{phy} + e_{chem} \tag{2}$$

Where

$e = \frac{\dot{E}}{\dot{m}}$ and $\dot{m}$ is the mass flow rate of the stream.

A. Physical Exergy

Physical exergy, known also as thermo mechanical exergy, is the work obtainable by taking the substance through reversible process from its initial state (T, P) to the state of the environment (T_0, P_0). The specific physical exergy is written as:

$$e_{phy} = (h - h_0) - T_0(S - S_0) \tag{3}$$

For perfect gas with constant C_p

$$e_{phy} = C_p(T - T_0) - T_0\left[C_p \ln\frac{T}{T_0} - R\ln\frac{P}{P_0}\right] \tag{4}$$

For solids and liquids when assuming constant specific heat C,

$$e_{phy} = C\left[(T - T_0) - T_0\left(\ln\frac{T}{T_0}\right)\right] - v_m(P - P_0) \tag{5}$$

Where v_m is the specific volume determined at temperature T_0.

B. Chemical Exergy

Chemical exergy is equal to the maximum amount of work obtainable when the substance under consideration is brought from the environmental state (T_0, P_0) to the dead state (T_0, P_0, μ_{0i}) by processes involving heat transfer and exchange of substances only with the environment.

When a substance does not exist in the reference environment, it must first react to reference substances in order to get in equilibrium with the environment. The reaction exergy at reference conditions equals the standard Gibbs energy change. So the overall specific chemical exergy term becomes:

$$e_{chem} = \sum_i x_i\left[e_{0i} + RT_0 \ln(x_i)\right] \tag{6}$$

Where x_i represents the molar fraction of component i, and e_{0i}, is standard chemical exergy.

The chemical exergy of real components can be computed from:

$$e_{chem} = \sum_i x_i\left[e_{0i} + RT_0 \ln(\gamma_i x_i)\right] \tag{7}$$

Where γ_i is the activity coefficient of component i

C. Simple Exergy Efficiency

The Simple exergy efficiency is the ratio of the total exergy leaving to the total exergy entering in the control volume.

$$\eta = \frac{E_{out}}{E_{in}} \tag{8}$$

D. Rational Exergy Efficiency of Different Components

The ratio of desired exergy output to the exergy used for that purpose is called as rational exergy efficiency.

$$\Psi = \frac{E_{desired\ output}}{E_{used}} \tag{9}$$

a. Adiabatic Compressor

The rational efficiency for an adiabatic compressor is given by

$$\Psi_C = \frac{E_{out} - E_{in}}{W_{in}} \tag{10}$$

Where W_{in} is work input of the compressor

b. Turbine

The rational exergy efficiency of turbine is defined as the ratio of the work output to the exergy decrease of the incoming and outgoing flows.

$$\Psi_T = \frac{W_{out}}{E_{out} - E_{in}} \tag{11}$$

Where W_{out} is work output of the turbine

c. Counter Flow Heat Exchanger

The rational exergy efficiency of counter flow heat exchanger is given by

$$\Psi_{HX} = \frac{\sum_J \Delta E_J^T}{\sum_K \Delta E_K^T} \tag{12}$$

Where, ΔE_J^T is thermal component of exergy gained by J^{th} stream

and ΔE_k^T is thermal component of exergy lost by K^{th} stream

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d. Distillation Column

The exergetic rational efficiency of a distillation column is used to understand the irreversibility available in the process takes place in it. The most useful definition for exergy efficiency of a cryogenic air distillation is based on the minimum work of separation. Exergetic rational efficiency of cryogenic distillation is given by

$$\Psi_{DIST} = \frac{W_{\min}}{W_{\min} + \Delta E_{loss}} \qquad (13)$$

e. Biomass Gasification

Biomass gasification is process of converting solid to gaseous fuel. Exergetic efficiency takes into account the entropy increase due to conversion of a solid to a gaseous fuel. Exergetic efficiency of gasifier is given by

$$\Psi_{BG} = \frac{E_{syngas}}{E_{biomass} + E_{oxygen} + E_{steam}} \qquad (14)$$

IV. Exergy analysis of cryogenic ASU integrated with biomass gasifier

In an energy analysis, based on the first law of thermodynamics, all forms of energy are considered to be equivalent. Generally, energy balances provide no information about internal losses like quality loss of energy. For example, the change of the quality of thermal energy as it is transferred from higher to lower temperature which is not displayed in an energy analysis. An exergy analysis, based on first and second law of thermodynamics, shows the thermodynamic perfection of a process, including all quality losses of materials and energy. Since real processes are irreversible, the total exergy flowing into any unit operation is greater than the total exergy flowing out, while some exergy is lost during process in unit operation. Within the constraints of some cost and other process considerations, one of the objectives of a process engineer is to minimize the total exergy loss of a process. The exergy analysis of various unit operations in cryogenic ASU integrated with biomass gasifier performed with the help of Aspen plus.

A. Multistage Compressor and Booster

The incoming air is compressed to 4.1 bar in multistage compressor subsequently one stream directly cooled in main heat exchanger and admitted to HP column and other pressurized in booster. Exergy loss caused due to compression of the stream from 1.03 bar to 4.1 bar which is estimated as 8.43 kW. In booster air is compressed to 50 bar and supplied to main heat exchanger for matching the cooling load. Exergy loss is taking place in these compressors due to compression which is estimated as 11.43 kW.

B. Main Heat Exchanger

The exergy losses are caused by temperature difference between the hot and cold streams and pressure losses. The rational efficiency of heat exchangers is defined as the exergy increase of the cold streams divided by the exergy decrease of the hot streams.

C. Expander

The expander is used to expand air from 5 bar to 1 bar and supplied directly to HP column. The power produced by expander is utilized by main compressor. Exergy loss in the expander is due to the irreversibility available in the process which is estimated as 13.36 kW.

D. Joule – Thomson (JT) Valves

JT valves are used to reduce the pressure by throttling process. There are three JT valves used in simulation flow sheet as shown in part-I of Fig.1. Exergy loss in JT_1, JT_2 and JT_3 estimated respectively as 0.026 kW, 1.283kW and 0.437 kW.

E. Distillation Columns

The heat transfer between reboiler of LP column and condenser of HP column cause exergy loss due to temperature difference. The exergy loss in LP column and HP column found as 89.915 kW and 95.25 kW respectively.

F. Biomass Gasifier

Exergy loss in biomass gasifier is caused due to conversion of solid to gaseous fuel. Biomass gasifier model is prepared in Aspen plus and simulated on the basis of Gibbs free energy minimization. The exergy loss is estimated as 80.53 kW.

V. Results and discussion

In this simulation, a total of 209.78 scmh of gaseous O_2 product with 96.2% purity is produced which is safely used for gasification application. Gaseous N_2 product with purity 99.9% is also produced at volumetric flow rate of 734 scmh. Heat duties of the reboiler of the LP column and condenser of the HP column are matched by calculator block in Aspen plus. The main compressor consumes 47.22 kW power and booster consumes 12.22 kW power, which is partially compensated by the power of 9.32 kW generated in the expander. The specific power consumption obtained is 0.2435 kW/scmh of O_2. The detail simulation results of cryogenic ASU are shown in Table II. Steady state simulation model of biomass gasifier in Aspen plus predicts the composition of syngas. Syngas composition for different biomass with oxygen as gasifying agent is shown in Table III. Exergy rational efficiencies of various unit operations are shown in Table IV.

VI. Conclusion

The simulation model of cryogenic ASU in Aspen plus produces oxygen with required purity and recovery. Oxygen is obtained with purity 96.2% which is economically suitable for biomass/coal gasification for getting syngas with a higher heating value. The specific power consumption of the plant obtained is 0.2435 kW/scmh of $O_{2,}$ which is lower as compared to conventional cryogenic ASU plants. The rational efficiency found in main heat exchanger, expander, distillation columns and compressors. Theses efficiencies are less due to exergy loss taking place in the unit operations. It is seen that air gasification produces a syngas with lower heating value, while O_2 and steam blown processes result in a syngas with a higher heating value. However, the use of oxygen does have other advantages such as operation at lower equivalence ratio, smaller equipment size of gasifier and downstream equipment, and possibly savings in compression cost of produced gas.

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TABLE II

SIMULATION RESULTS OF CRYOGENIC ASU

Parameters	FEED	$GASN_2$	$GASO_2$	LM1
Temperature(K)	95.5	300.1	302.8	283.1
Pressure (bar)	4.1	1.1	1.15	50
Vapor Fraction	0.9	1	1	1
Mass Fraction				
N_2	0.755	0.998	5 ppb	0.755
O_2	0.232	18 ppm	0.953	0.232
Ar	0.013	0.002	0.047	0.013
Mole Flow (scmh)				
N_2	663.765	780.900	TRACE	114.792
O_2	178.33	0.012	209.78	30.814
Ar	7.905	1.088	8.212	1.367
Mole Fraction				
N_2	0.781	0.999	6 ppb	0.781
O_2	0.210	16 ppm	0.962	0.21
Ar	0.009	0.001	0.038	0.009

TABLE III

SYNGAS COMPOSITION OF VARIOUS FEED STOCKS

Syngas composition (mole %)	Indian coal		Rice husk	
Gasifying agent	Air	O_2	Air	O_2
H_2	8.8	15.3	22.9	36.5
CO	41.8	60.1	18.4	21.8
CO_2	0.623	0.003	13.0	20.2
H_2O	0.018	0.492	8.3	19.9
CH_4	17.3	0.23	0.8	0.6
N_2	32	0.8	36.6	0.4
CV (MJ/kg)	12.59	19.55	5.49	9.14

TABLE IV

RATIONAL EFFICIENCIES OF VARIOUS UNIT OPERATIONS

Unit operations	Rational efficiency
Multi stage compressor(C1)	64.43%
Booster(C2)	63.05%
Sub cooler(SUBCOL)	88.19%
JT1	--
JT2	--
JT3	--
Main heat exchanger (MHX)	56.41%
Expander(EXP)	50.22%
HP column	50.24%
LP column	54.01%
Biomass gasifier	72%

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