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ON A NUMERICAL MODLE FOR GASIFICATION OF BIOMASS MATERIALS

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Abstract: *Thermochemical equilibrium modeling is the basis of the numerical method implemented in this study to predict the performance of a downdraft biomass gasifier. To validate the model, a close agreement is shown between numerical and experimental results. Five different biomass materials of five major families are tested using the model and olive pit is shown to be the most energetic one. The effects of oxygen enrichment and pressure on gasification characteristics are investigated. These characteristics include composition and calorific value of the produced synthetic gas (syngas), as well as cold gas efficiency and temperature of the gasification process. Increasing oxygen enrichment from 21% (as in atmospheric air) to 100%, results in a considerable increase of 118% in syngas calorific value. Gasification under pressure makes a slight increase in calorific value and temperature. Increasing gasification pressure is shown to be economically more feasible than increasing the syngas pressure in downstream equipments.*

Key Words: ***Renewable Energy / Biomass / Syngas / Gasification / Thermochemical Equilibrium / Numerical Modeling /***

1. INTRODUCTION

Controversial projections about natural gas reserves depletion by the 1980s and 1990s, the oil embargo of 1973, and more restrictive and stringent environmental standards provided incentive for both governments and industries to explore and promote the commercialization of new sources of fuel, such as biomass, and also new technologies in order to utilize them [1]. The term biomass covers a broad range of materials that have one thing in common, they are all derived from recently living organisms, such as agricultural and forestry wastes, as well as purpose-grown materials as biomass. The use of biomass as a fuel is largely restricted to the use of by-products from forestry and the paper and sugar industries. Nonetheless, its use is being encouraged as part of a strategy for CO_2 abatement [2]. Reuse and recycling, composting, incineration, and land filling are four main categories of acceptable biomass handling options from which the last two are the most frequently used methods [3]. More recently, gasification of biomass materials has also been introduced as a thermochemical conversion; a process to convert carbonaceous materials to a synthetic gas (syngas). One of the attractive features of this technology includes the ability to produce a clean syngas product that can be used for either generating electricity or producing chemicals.

For the complete combustion of biomass, the theoretical amount of air required (stoichiometric quantity) is 6 to 6.5 kg air/kg biomass. The final products are CO_2 and H_2O. In gasification, biomass is subjected to partial pyrolysis under sub-stoichiometric conditions with the air quantity being limited to 1.5 to 1.8 kg air/kg biomass. The resultant mixture of gases produced during gasification process contains CO and H_2 and is combustible. The raw syngas also contains tar and particulate mater, which have to be removed depending on the application. The fuel gas produced has a relatively low calorific value (3 to 12 MJ/m^3) in comparison with that of natural gas (34 MJ/m^3); however, this product can be combusted at a relatively high efficiency and with good degree of control without emitting smoke.

Biomass gasifiers are complex equipments that require a lot of time to be mounted and to be put in operation; make it difficult to explore various working conditions such as moisture content, etc. As a result, some mathematical models were made to predict the performance of the gasifiers [4-6]. The equilibrium model has been used by many researchers for the analysis of the gasification process. Although, thermochemical equilibrium, in reality, never takes place during gasification [7], many works were performed to demonstrate the applicability of the equilibrium models to this process. These models are especially good at the high temperatures that occur on the entrained flow gasifiers, where the reaction temperatures are above 1500K [8]. Some models were based on the minimization of Gibbs free energy [9-10] while others used the idea of equilibrium constants.

Altafini et al. [6] simulated a biomass gasifier, based on minimizing the Gibbs free energy. The biomass gasification process was also modeled by Zainal et al. [11]. Lapuerta et al. [12] predicted the producer gas composition as a function of the fuel/air ratio by means of an equilibrium model. A description of a two-zone model in a downdraft gasifier was adapted by Jayah et al. [4] and Schuster et al. [13]. An experimental study was also described by Zainal et al. [14].

In this paper, a biomass gasification process is modeled using a thermochemical equilibrium with equilibrium constants. Validation of the numerical model is the first issue, which is done via comparison between calculated results and experimental data [4,6]. The effect of ultimate analysis on the calorific value is studied for five different common biomass materials of five major families. The influence of oxygen enrichment and pressure on gasification characteristics is also discussed. These characteristics are the syngas composition, gasification temperature, calorific value and the cold gas efficiency.

2. MATHEMATICAL MODEL

The main assumptions of the developed model are as follows: the gasifier reactor is assumed to be adiabatic and the residence time of the reactants is supposed to be high enough to reach chemical equilibrium. In addition, all carbon in the biomass is assumed to be gasified and; therefore, the formation of char and tar is neglected. The global gasification reaction can be written as follows:

$$CHxOyNz + wH_2O_{(liq)} + sH_2O_{(vap)} + m(O_2 + 3.76N_2) = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + (z/2 + 3.76m)N_2 \qquad (1)$$

where x, y, and z are numbers of atoms of hydrogen, oxygen, and nitrogen per one atom of carbon in the feedstock; respectively, and w, m, and s are molar quantity of moisture, air/oxygen, and steam, respectively. All inputs on the left-hand side of Eq. 1 are defined at 25ºC. On the right-hand side, n_i is the number of moles of species i, which is an unknown. Molar quantity of water per one kmol of biomass can be written as [11]:

$$w = \frac{M_{bm} \times MC}{M_{H_2O} \times (1 - MC)} \qquad (2)$$

where M_{bm} and M_{H2O} are the masses of the biomass and water; respectively, and MC is the moisture content. Air/fuel ratio can be calculated as ($\alpha + 0.25\beta - 0.5\gamma$) for a fuel with a chemical formula of $C_\alpha H_\beta O_\gamma N_\zeta$ [15]. During the gasification process, between 30% and 70% of stoichiometric air is used; therefore, we assume m to be a fraction of the calculated stoichiometric air.

To obtain the five unknown species of the syngas, five equations are required, which are generated using mass balance and equilibrium constant relationships. Considering the global gasification reaction in Eq. 1, the first three equations are formulated by balancing each chemical element consisting of carbon, hydrogen, and oxygen. The remaining two equations are obtained from the equilibrium constants of the reactions that occur in the gasification zone which are given as:

$$\text{Boudouard reaction}: C + CO_2 = 2CO \qquad (3)$$

$$\text{Water-gas reaction}: C + H_2O = CO + H_2 \qquad (4)$$

$$\text{Methane reaction}: C + 2H_2 = CH_4 \qquad (5)$$

Higman et al. [2] showed that Eqs. 3 and 4 can be combined to give the water–gas shift reaction:

$$\text{Water-gas shift reaction}: CO + H_2O = CO_2 + H_2 \qquad (6)$$

Since we are going to analyze the effect of pressure on gasification characteristics, it is necessary to study the relation between pressure and equilibrium constants. A reaction moves in the direction of decreasing chemical potential, reaching equilibrium only when the potential of the reactants equal that of the products [16]. Thus the criterion for the equilibrium at constant T and P is:

$$(dG)_{T,P} = 0 \qquad (7)$$

which can be used to determine the relationship between the Gibbs free energy (G) and the equilibrium partial pressure of a product mixture. For the present model, in addition to an assumption of thermodynamic equilibrium, all gases are assumed to be ideal. Therefore, there are no forces of interactions between the molecules except at the instant of reaction; thus, each gas acts as if it was in the container alone. An equilibrium reaction with arbitrary products is written as:

$$aA + bB + ... \leftrightarrow rR + sS + ... \qquad (8)$$

where A, B, ..., R, S, ... represent the involving substances and a, b, ..., r, s, ... are the stoichiometric coefficients. Under the ideal gas assumption, one may neglect the free energy of mixing. Based on the concept of the Gibbs free energy and since the standard state pressure for a gas is $P°=1$ atm, we have:

$$(G - G^\circ) = (H - H^\circ) - T(S - S^\circ) \qquad (9)$$

where H is the total enthalpy. For an ideal gas, the enthalpy is not a function of pressure; thus, (H-$H°$) must be zero. The relation of the entropy (S) to the pressure is:

$$S - S^\circ = -R\ln(p/p^\circ) \qquad (10)$$

where R is the universal gas constant. Hence:

$$G(T,p) = G^\circ + RT\ln(p/p^\circ) \qquad (11)$$

In this case, p_i is the partial pressure of a particular gaseous component and has the following relationship to the total pressure P:

$$p_i = (n_i / \sum_i n_i)P \qquad (12)$$

where ($n_i / \Sigma n_i$) is the mole fraction of gaseous species i in the mixture. Thus, Eq. 11 becomes:

$$G(T,P) = \sum_i n_i[G_i^\circ + RT\ln(p_i / p^\circ)] \qquad (13)$$

As discussed above, the criterion for equilibrium is $(dG)_{T,P} = 0$. Taking the derivative of G in Eq. 13 yields:

$$\sum_i G_i^\circ dn_i + RT\sum_i (dn_i)\ln(p_i / p^\circ) + RT\sum_i n_i(dp_i / p^\circ) = 0 \qquad (14)$$

Since the total pressure is constant, $\Sigma\, dp_i = 0$. Therefore, the last term of the left-hand side of Eq. 14 is equal to zero. The standard state free energy changes as:

$$-\Delta G^\circ = a\Delta G_A^\circ + b\Delta G_B^\circ + ... - r\Delta G_R^\circ - s\Delta G_S^\circ - ... \qquad (15)$$

Since the standard state pressure p^0 is 1 atm, the condition for equilibrium becomes:

$$-\Delta G^0 = RT\ln(p_R^r p_S^s / p_A^a p_B^b) \qquad (16)$$

where p_i, the partial pressures, are measured in atmospheres. Then the equilibrium constant at constant pressure can be defined as:

$$K_p \equiv p_R^r p_S^s / p_A^a p_B^b \qquad (17)$$

Therefore:

$$-\Delta G^\circ = RT\ln K_p, \quad \ln K_p = -\Delta G^\circ / RT \qquad (18)$$

where K_p *is not a function of the total pressure, but rather a function of temperature alone*. Using the relationship between partial pressure p and total pressure P (Eq. 12), the definition of the equilibrium constant can be written as:

$$K_p = (n_R^r n_S^s / n_A^a n_B^b)(P / \sum n_i)^{r+s-a-b} \tag{19}$$

The dependence of ΔG° on temperature can be written as follows:

$$\frac{d(\Delta G^\circ / RT)}{dT} = \frac{-h_f^\circ}{\widetilde{R}T^2} \tag{20}$$

where h_f° is the enthalpy of formation with a value of zero for all chemical elements in a reference state. Therefore, based on Eq. 18 we will have:

$$\frac{d \ln K_p}{dT} = \frac{h_f^\circ}{\widetilde{R}T^2} \tag{21}$$

Since the heat of formation is a function of T, Eq. 21 can be integrated as follows:

$$\ln K_p = \int \frac{h_f^\circ}{\widetilde{R}T^2} dt + I \tag{22}$$

The temperature of the gasification zone needs to be determined in order to calculate the equilibrium constants from Eq. 18. For this reason, a balance of either energy or enthalpy is performed on the gasification process usually assumed to be adiabatic. If the temperature in the gasification zone is T and that of the inlet state is assumed to be 298K, the enthalpy balance for this process can be written as:

$$\sum_{j=react} n_j h_{f,j}^\circ = \sum_{i=prod} n_i (h_{f,i}^\circ + \Delta h_{T,i}^\circ) \tag{23}$$

where Δh_T° represents the enthalpy difference between any given state and the reference state. It can be approximated by:

$$\Delta h_T^\circ = \int_{298}^{T} \overline{C}_p(T) dT \tag{24}$$

where $\widetilde{C}_p$ is the specific heat at constant pressure which is only a function of temperature. It is defined by an empirical relation as [17]:

$$\overline{C}_p(T) = C_1 + C_2 [\frac{C_3 / T}{\sinh(C_3 / T)}]^2 + C_4 [\frac{C_5 / T}{\sinh(C_5 / T)}]^2 \tag{25}$$

When the equilibrium constants are defined, a system of equations will be obtained that need to be solved. Because of the non-linear nature of some of the equations, the Newton–Raphson method is used, which can be solved with an interative procedure. The procedure starts with an initial guess for the gasification temperature. The set of equations are then solved to obtain the syngas composition which in turn is used to determine the new gasification temperature. This iterative procedure continues until the gasification temperature does not change within a desired limit in successive iterations.

3. RESULTS AND DISCUSSION

In order to validate the implemented model, obtained syngas gas composition is first compared to that of the experiments performed by Jayah et al. [4] and Altafini et al. [6]; this comparison is shown in Table 1. The slight differences in components may be attributed to the simplifying assumptions of the model such as: considering all gases to be ideal, assuming gasifier to be adiabatic, and assuming no char or residue in the gasification process. As seen from the table, the model results compare reasonably well with measurements.

Table 1. *Comparison between model predictions and measurements for two biomass gasification processes.*

	Reference [4][a]		**Reference [6]**[b]	
	Exp	**Model**	**Exp**	**Model**
H_2 (%vol)	17.2	15.8	14.0	15.2
CO (%vol)	19.6	20.0	20.1	22.3
CO_2 (%vol)	9.9	11.4	12.0	9.8
CH_4 (%vol)	1.4	0.7	2.31	0.59
N_2 (%vol)	51.9	51.9	50.7	51.8
CV (MJ/m^3)		4.82	5.27	5.01
RMS[c] **Err**	0.998		1.56	

a) *Rubber Wood –with 18.5% moisture content*
b) *Sawdust –with 10% moisture content*
c) $RMS = \sqrt{\frac{\sum_i^N (Experiment_i - Model_i)^2}{N}}$

In order to compare various biomass sources of energy, gasification of five different samples are simulated under the same conditions (biomass with zero moisture content and setting air ratio equal to 0.35 of the stoichiometric ratio) to evaluate their syngas calorific values. These samples were selected across five major groups of biomass materials [18] consisting of grasses and straws; wood fuels; urban waste fuels; wood fuel blends; nuts, pits and shells. The results of the simulations are shown in Fig.1. As seen from the figure, olive pits are found to produce the highest calorific value (5.9 MJ/m^3). Ultimate analysis of olive pits is 52.8%C, 6.69%H, 38.29%O, 0.45%N, 0.05%S and a high heating value (*HHV)* of equal to 481.580 MJ/kmol.

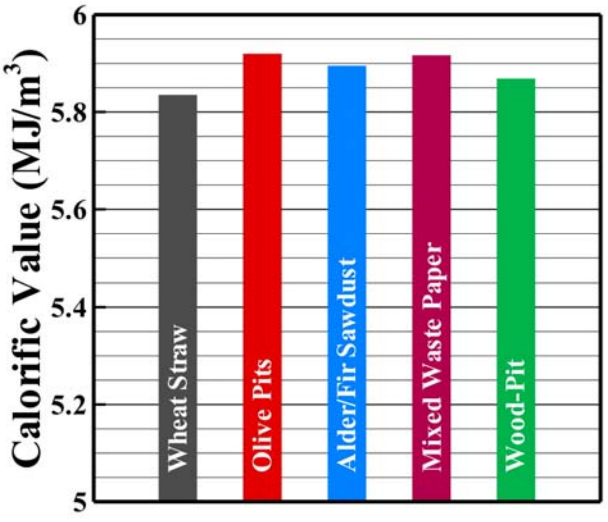

Fig. 1. Comparison between calorific values obtained via gasification of five different biomass materials

Parametric studies reported in the literature [4-6] mainly have concentrated on analyzing the effect of moisture content on gasification characteristics and fuel gas composition. The effects of steam injection and air preheating have rarely been reported [19]. In this paper, specifically, the effects of oxygen enrichment and pressure on gasification process are studied. It should be mentioned that injecting oxygen and increasing gasification pressure are mainly applied in industrial/semi-industrial gasification projects. The reason is the capital-intensive facilities required (such as compressors) for these techniques.

The effect of increasing oxygen available in gasifying agent (air) on calorific value of syngas and gasification temperature is shown in Fig. 2. In the simulation, the feed of gasifying agent was limited to 0.35 of that of the stoichiometric value, the gasification pressure was one atmosphere and the moisture content was zero. As it can be observed in the figure, an increase of oxygen enrichment from 21% (oxygen ratio in atmospheric air) to 100% results in a 50% increase of gasification temperature. Also syngas calorific value increases from 5.23 MJ/m^3 to 11.42 MJ/m^3; a considerable increase of 118%. The reason for this variation can be seen clearly in Fig. 3 where gas composition variation is shown against oxygen enrichment. Volumetric percents of energetic gases that contribute in the procedure of syngas calorific value calculation, including CO and H_2, are increased by 79% and 143%; respectively. Although the amount of CH_4, as another energetic gas is reduced, but its low volumetric percent makes its effect negligible. It must be reminded that in the process of biomass gasification with air, the maximum calorific value that can be reached is 6 MJ/m^3. Obtaining calorific values close to 12 MJ/m^3 (by increasing oxygen enrichment) makes the syngas suitable for applications that take the advantage of high calorific value gases, such as gas turbines.

Figures 4 and 5 display the effect of gasification pressure on calorific value and temperature, and gas composition; respectively. In the simulation, the pressure ranged from 1 atm to 60 atm. As it can be seen in Fig. 4, the pressure increase made only 0.94% increase in syngas calorific value and 8.4% increase in temperature. Also, an increase in CH_4 and CO_2 contents with increasing pressure can be seen in Fig. 5. The contents of CO and H_2, however, were reduced with pressure increase. A large increase in CH_4 content from 0.17 to 2.3 %vol, leads to an increase in syngas calorific value in spite of reduction in H_2 and CO contents. The reduction of CO and H_2 is the certain cause for the reduction of cold gas efficiency (the second law of thermodynamics efficiency) observed in Fig. 6. This figure also reveals that oxygen enrichment has a small influence on the cold gas efficiency. Based on the above discussion, the gasification under pressure has no significant effects on gasification characteristics. However, this technique is economically preferred over pressurizing the syngas in downstream equipments. On a performed survey [2], the energy required to provide 100,000 m^3/h sygas at 45 bar (44.4 atm) was calculated by following two methods:

a) gasifying at relatively low pressure (5 bar) and compressing the gas in downstream equipment,
b) compressing the feedstock to 55 bar (allowing for the pressure drop in the system) and gasifying at the higher pressure.

The oxygen was assumed to be available at atmospheric pressure in both cases. The energy required for gas compression in the second method was found to be 0.25 of that of the first method.

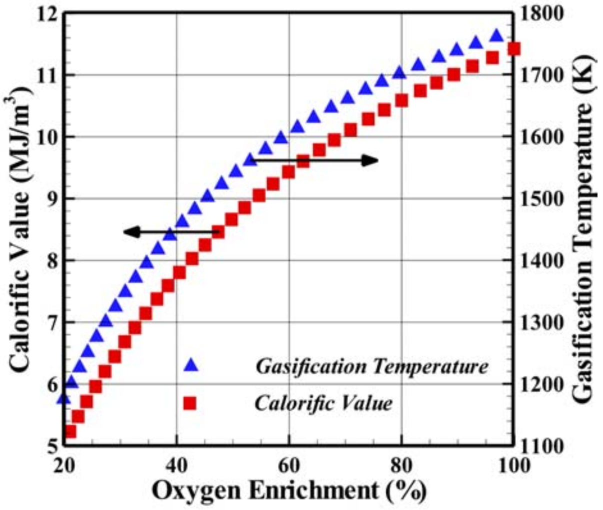

Fig. 2. Effect of oxygen enrichment on gasification temperature and calorific value of the syngas

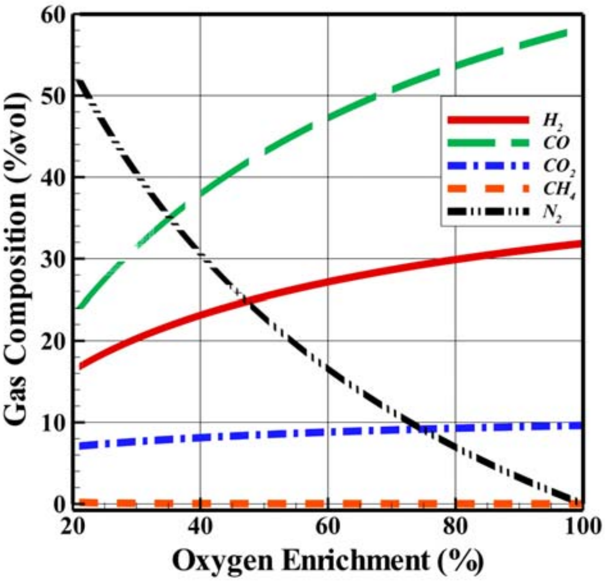

Fig. 3. Effect of oxygen enrichment on gas composition

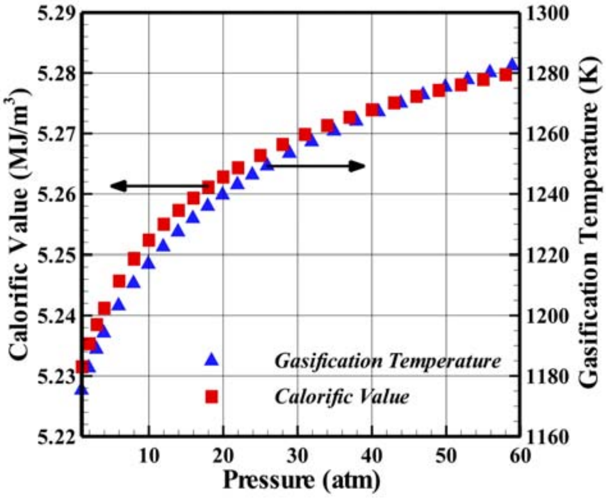

Fig. 4. Influence of pressure on gasification temperature and calorific value of the syngas.

4. CONCLUSSION

A thermochemical equilibrium model was developed for a biomass gasifier in order to calculate the composition of the syngas and investigate the effect of processing parameters on gasification characteristics. The predicted results agreed well with those of the experiments available in the literature. The model was then employed to evaluate the capability of different biomass materials to produce energy. Among five different biomass materials, olive pits had the highest calorific value. The effects of oxygen enrichment and pressure on gasification characteristics were analyzed. Although increasing the oxygen enrichment led to an increase in temperature (not favored), it was found to be a reliable tool to increase syngas calorific value significantly reaching a remarkable value of 11.42 MJ/m^3. Gasifying under pressure increased the syngas calorific value; it was also shown to be a more preferable technique over compressing the syngas in downstream equipment economically. The developed model in this study can be used to simulate/optimize gasification of different types of biomass materials and predict the effect of processing parameters.

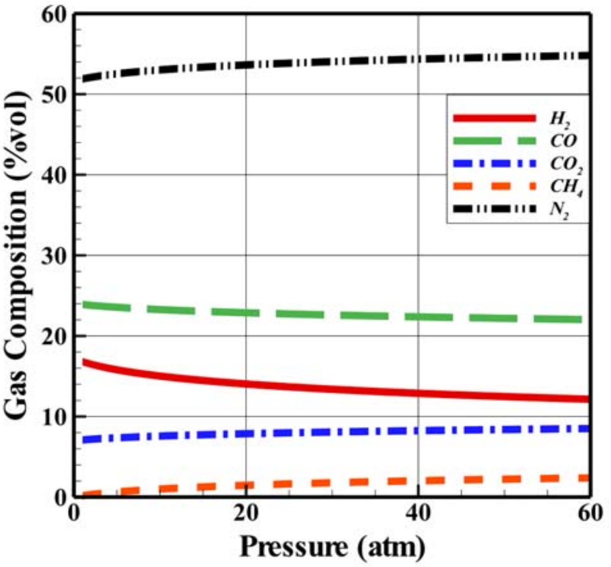

Fig. 5. Influence of pressure on gas composition

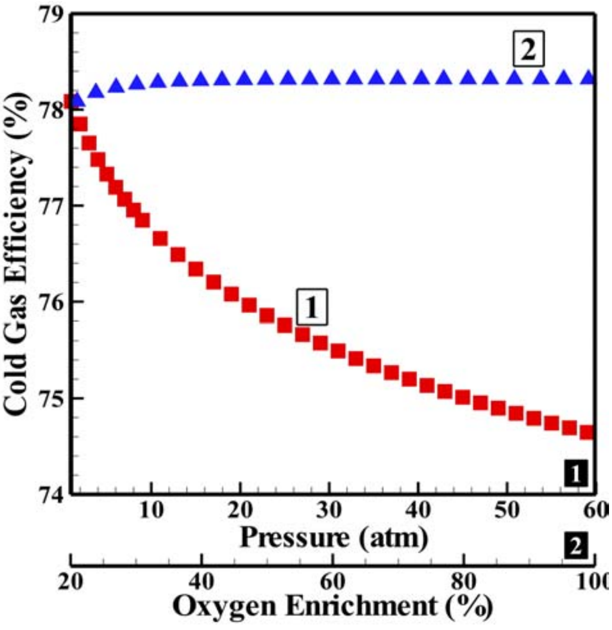

Fig. 6. Effect of oxygen enrichment and pressure on cold gas efficiency

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