

On a Numerical Model for Gasification of Heavy Fuel Oils: An Alternative Technology for Processing Refinery Residues

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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 heavy fuel oil gasifier. Numerical results are shown to be in good agreement with those of the experiments. The model provides the corresponding synthetic gas (syngas) composition and calorific value, the gasification temperature, cold gas efficiency, and the carbon conversion efficiency. The effect of important processing parameters including equivalence ratio, air inlet temperature, gasification pressure, and the type of gasifying agent is also studied. It is shown that the gasification of heavy fuel oil can lead to calorific values as noticeable value as 18 MJ/m³ and efficiencies as high as 90%. 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.

Keywords: Gasification technology, Numerical modeling, Thermochemical equilibrium, Heavy fuel oil

Introduction

It has been shown that the quality of the crude oils produced around the world is deteriorating [1]. At a typical refinery, this trend means the production of more residual high-sulfur/metal heavy fuel oil. In turn, this means reduced revenue for the refiner because the markets for heavy fuel oil are rapidly shrinking as a result of increasingly stringent environmental regulations. The challenge of refiners, therefore, is to process heavier crude oils without producing a product that is becoming much less marketable.

In our country, based on a survey reported for 2004 [2], heavy fuel oils, on average, constitute 32% of volume of products of Iranian refineries and 33.7% per barrel of crude oil is converted to heavy fuel oil [3]. Considering the price per barrel of heavy fuel oil, which roughly equals to half of crude oil, and high rate of consumption of heavy fuel oils in Iran (35 million liters per day), any try to reduce the production volume of residual bottom products in refineries is economically and environmentally profitable.

There are refining technologies available to meet this challenge such as solvent deasphalting, residue

hydrotreating, and residue fluid catalytic cracking. However, these capital-intensive conversion techniques can still leave the refiner with a residual bottom product that, while reduced in volume, contains substantial amounts of sulfur and heavy metals.

On the other hand, most of the facilities which historically employ heavy fuel oil combustors - industrial plants and similar facilities - suffer from corrosion. The high sulfur content of heavy fuel oil - up to 3% by weight in some extreme cases - has a corrosive effect on many heating systems, shortening their lifespans and increasing the polluting effects.

Yet there is another solution to the problem of heavy fuel oils that refineries/industries in various parts of the world are looking at with considerable interest - gasification technology.

In the case of refineries, depending on the refiner's particular processing configuration and product values, gasification can be a cost effective way to reduce inventories of heavy bottom products virtually to zero. Concerning industrial plants, from a technical standpoint, as well as environmental point of view, gasification offers several advantages over combustion of heavy fuel oils. Negative effects of sulfur and nitrogen oxides, as well as particulate from gasification are reduced significantly due to the cleanup of syngas. Sulfur in gasifier feed is converted to H_2S , and nitrogen in the feed is converted to diatomic nitrogen (N_2) and NH_3 . Both H_2S and NH_3 are removed in downstream processes, producing a clean syngas. Therefore if the resulting clean syngas is combusted in a furnace or gas turbine, the production of sulfur and nitrogen oxides are reduced significantly.

Gasification is a thermochemical process to convert carbonaceous materials to a clean synthetic gas (syngas); mainly consisting of CO and H_2 . The resulting syngas can be converted into products such as hydrogen, methanol, formaldehyde, and ammonia. Further, the IGCC¹ approach combines gasification with the production of electric energy. The syngas can be used to fuel a gas turbine to produce electricity in a very efficient and economical manner.

It should be mentioned that gasification is *not* combustion. A combustion process needs stoichiometric feed of air/oxygen, while gasification is performed at sub-stoichiometric conditions (30% to 70% of stoichiometric air/oxygen). Sometimes, nitrogen and/or steam are also injected in order to control the gasification condition and volume of products. As a

result, the products/byproducts of combustion and gasification are totally different [4].

The many advantages of gasification over combustion make it feasible to review the possibilities of syngas production as an alternative technology for processing heavy oil residues with their high sulphur/metal contents while simultaneously not exceeding the environmental red lines.

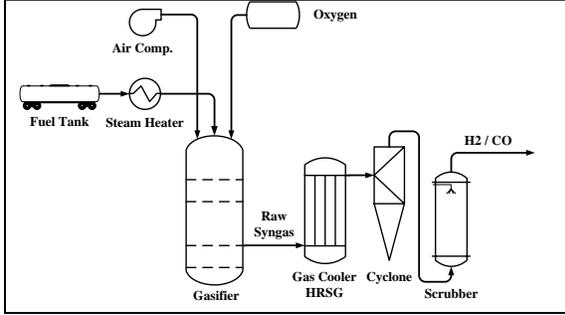


Figure 1. Systematic diagram of heavy fuel oil gasifier

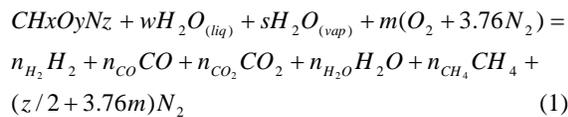
In this paper, a heavy fuel oil gasification process is modeled using thermochemical equilibrium modeling. Validation of the numerical model is the first issue, which is done via comparison between calculated results and experimental data [5]. The influence of equivalence ratio (virtual air/stoichiometric air), gasification pressure, the type of gasifying agent (air/oxygen), and air preheating on gasification characteristics is also discussed. These characteristics are the syngas composition, gasification temperature, syngas calorific value, cold gas efficiency and the carbon conversion efficiency.

Mathematical Model

A zero dimensional model presented in this paper is based on thermochemical equilibrium of the process using equilibrium constants. Equilibrium modeling has been used frequently in the past for biomass gasification [6,7,8,9]; the use of this model for gasification of liquid fuels, however, is not reported.

The main assumptions of the developed model are as follows: the residence time of the reactants is supposed to be high enough to reach chemical equilibrium, the gasifier is assumed to be adiabatic, all gases are supposed to be ideal, all carbon in heavy fuel oil is assumed to be gasified and, therefore, the formation of char is neglected, ash in heavy fuel oil is inert and does not participate in chemical reactions, and the syngas is comprised of H_2 , CO , CO_2 , H_2O , CH_4 , and N_2 ; tar was not taken into account in the simulation.

The global gasification reaction can be written as follows:



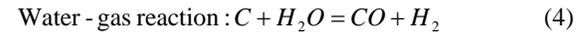
where x , y , and z are numbers of atoms of hydrogen, oxygen, and nitrogen per one atom of carbon in the feedstock; respectively, and w , m , and s are the amounts of water, air, and steam per one kmol of feedstock, respectively. All inputs on the left-hand side of Eq.(1)

are defined at $25^\circ C$. On the right-hand side, n_i is the number of moles of the species i which is also unknown. Molar quantity of water per one kmol of heavy fuel oil can be written as:

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

where M_{HFO} and M_{H_2O} are the masses of the heavy fuel oil and water; respectively, and MC is the water content. Air/fuel ratio can be calculated as $(\alpha + 0.25\beta - 0.5\gamma)$ for a fuel with a chemical formula of $C_\alpha H_\beta O_\gamma N_\xi$ [10]. During the gasification process, heavy fuel oil is subjected to partial pyrolysis under sub-stoichiometric conditions. Therefore, we assume m (equivalence ratio) to be a fraction of the calculated stoichiometric air.

To obtain the five unknown species of the producer gas, 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 constant of the reactions that occur in the gasification zone which are given as:



Methanation reaction or Steam reforming:



Higman and van der Burgt [11] showed that Eqs.(3) and (4) can be combined to give the water-gas shift reaction as:



Therefore, the equilibrium constants, which are mere functions of temperature, for the methanation and the water-gas shift reactions can be written based on the following:

$$K = \prod_i (x_i)^{v_i} \left(\frac{P^\circ}{n_{total}} \right)^{\sum v_i} \quad (7)$$

where x_i is mole fraction of the species i in the ideal gas mixture, v is the stoichiometric number, P° is the standard pressure (1atm) and n_{total} is the total number of moles of produced gas. As a result, the equilibrium constants for the water-gas shift and the methanation reactions will be as follows:

$$k_1 = \frac{(n_{CO_2})(n_{H_2})}{(n_{CO})(n_{H_2O})} \quad (8)$$

$$k_2 = \frac{4(n_{CH_4})(n_{H_2O})}{P^\circ (n_{CO})(n_{H_2})^3} \quad (9)$$

The values of the equilibrium constants, which are mere functions of temperature, can be calculated using the Gibbs free energy:

$$\ln k = \frac{-\Delta G_T^\circ}{RT} \quad (10)$$

where \tilde{R} is the universal gas constant and ΔG_f° is the standard Gibbs function of formation. The dependence of ΔG° on temperature can be written as follows:

$$\frac{d(\Delta G^\circ / RT)}{dT} = \frac{-h_f^\circ}{\tilde{R}T^2} \quad (11)$$

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.(11) we will have:

$$\frac{d \ln k}{dT} = \frac{h_f^\circ}{\tilde{R}T^2} \quad (12)$$

Since the heat of formation is a function of T, Eq.(12) can be integrated as follows:

$$\ln k = \int \frac{h_f^\circ}{\tilde{R}T^2} dt + I \quad (13)$$

The amounts of ΔG° and h_f° can be found in chemical engineering handbooks [12].

Jarungthammachote et al. [13] multiplied k [see Eqs. (8) and (9)] by a factor to improve the performance of the model. The same factor is used in this model. The temperature of the gasification zone needs to be determined in order to calculate the equilibrium constants [Eq.(10)]. For this reason, a balance of either energy or enthalpy is performed on the gasification process. 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:

$$\sum_{j=react} n_j (h_{f,j}^\circ + \Delta h_{T,j}^\circ) = \sum_{i=prod} n_i (h_{f,i}^\circ + \Delta h_{T,i}^\circ) \quad (14)$$

where $\Delta h_{T,i}^\circ$ represents the enthalpy difference between any given state and the reference state. It can be approximated by:

$$\Delta h_{T,i}^\circ = \int_{298}^T \bar{C}_p(T) dT \quad (15)$$

where $\bar{C}_p(T)$ is the specific heat at constant pressure which is only a function of temperature. It is defined by empirical relations for fuel [13] and gasification products [14], respectively, as:

$$\bar{C}_p(T_{fuel}) = 0.76 + 0.000335(T_{fuel}) \quad (16)$$

$$\bar{C}_p(T) = C_1 + C_2 \left[\frac{C_3/T}{\sinh(C_3/T)} \right]^2 + C_4 \left[\frac{C_5/T}{\sinh(C_5/T)} \right]^2 \quad (17)$$

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 together with particular convergency strategies is used which can be solved with an iterative procedure. The procedure starts with an initial guess for the gasification temperature. The set of equations are then solved to obtain the producer gas 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 certain limit (much less 1 K) in successive iterations.

Results and Discussion

A residual fuel oil is any petroleum-based fuel which contains the undistilled residue from atmospheric or vacuum distillation of crude oil and may be called Bunker Fuel Oil, No. 6 Fuel Oil, or heavy Fuel Oil [15]. Heavy fuel oil must, in fact, be heated to 65°C– 120°C before it can be easily pumped. The flash point of most blends of heavy fuel oil is, incidentally, about 65.56°C. Important physical and chemical properties of heavy fuel oil, used in this paper, are shown in table 1.

Table 1. Heavy fuel oil properties [16-17]

Physical Properties	
Viscosity (mm ² /s @ 30°C)	2400
Density (Kg/m ³)	985
Flash Point (°C)	65
HHV (MJ/Kg)	40.14
Ultimate Analysis (As Rec'd)	
Carbon (Wt.%)	85.0
Hydrogen (Wt.%)	10.0
Oxygen (Wt.%)	0.0
Nitrogen (Wt.%)	0.4
Sulfur (Wt.%)	1.4
Ash Content (Wt.%)	0.2
Water (Wt.%)	3.0

To validate the model, we select a case (liquid fuel) for which measurements are available in the literature. Ashizawa et al. [5] studied gasification characteristic of OrimulsionTM in a research scale gasifier.

The word of Orimulsion is derived from the word combination of Orinoco and emulsion. It is a bitumen (coal) in-water emulsified fuel produced in Orinoco Belt of eastern Venezuela. The Orinoco bitumen is mixed with water to create an emulsion of approximately 30% water and 70% bitumen, with addition of small amounts of surfactant [18]. It is currently priced to be competitive with internationally traded coal and relatively easy and safe to produce, transport, handle and store. Furthermore it shows good ignition capability with moderate combustion characteristics.

The physical properties and chemical composition of OrimulsionTM are very close to those of the heavy fuel oil (table 2). Operating conditions are exactly simulated according with those of experiment. Table 3 shows a comparison between the results of the model and those of the experiments. Close agreement between the two results validates the developed model and its underlying assumptions.

Table 2. Orimulsion properties [5-19]

Physical Properties	
Viscosity (mm ² /s @ 30°C)	230
Density (Kg/m ³)	1015
Flash Point (°C)	>100
HHV (MJ/Kg)	29.76
Ultimate Analysis (As Rec'd)	
Carbon (Wt.%)	60.0
Hydrogen (Wt.%)	7.35
Oxygen (Wt.%)	0.39
Nitrogen (Wt.%)	0.45
Sulfur (Wt.%)	2.81
Ash Content (Wt.%)	0.178
Water (Wt.%)	28.8

Table 3. Comparison between numerical results and measurements [5] for syngas produced from Orimulsion™.

	Syngas produced from Orimulsion™	
	Experimental	Numerical
H ₂ (vol.%)	39.4	37.67
CO (vol.%)	38.7	37.47
CO ₂ (vol.%)	8.67	11.29
H ₂ O (vol.%)	11.85	11.62
CH ₄ (vol.%)	0.08	1.92
RMS ^a Err.	1.72	

$$a) \text{ RMS} = \sqrt{\frac{\sum_{i=1}^N (\text{Experiment}_i - \text{Model}_i)^2}{N}}$$

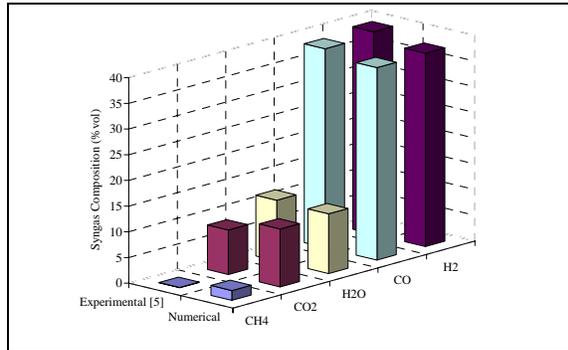


Figure 2. Comparison between numerical and experimental results

After gaining confidence in authenticity of developed numerical algorithm, initial data pertinent to heavy fuel oil is introduced to model and gasification process is simulated. A typical result of gasification simulation procedure together with corresponding operating conditions is presented in table 4. Reaching a calorific value equal to 12MJ/m³ seems to be satisfying.

Table 4. A typical result of gasification simulation procedure and operating conditions

Operating Conditions		
Equivalence Ratio		0.4
Gasification Pressure (atm)		10.0
Gasifying Agent		Air
Air Inlet Temperature (K)		1000.0
Results		
H ₂ (vol.%)		37.41
CO (vol.%)		54.0
CO ₂ (vol.%)		4.11
H ₂ O (vol.%)		3.21
CH ₄ (vol.%)		1.17
HHV (MJ/m ³)		12.0

Equivalence ratio – the ratio of virtual air/oxygen to stoichiometric air/oxygen – is a key parameter in gasification process. Due to the fact that, equivalence ratio distinguishes between gasification and combustion processes. As it was discussed before, the air/oxygen stream of a gasification process should be between 30% and 70% of the stoichiometric air/oxygen. If this portion is increased, the process nears the usual combustion with a tendency to produce CO₂ and H₂O (dominant

products of combustion process). This will increase the temperature and considerably decrease the calorific value of the produced gas. Reduction in syngas calorific value is the immediate outcome of reduction in volume of production of energetic gases, including H₂, CO, and CH₄. The results obtained via numerical model support the above logical discussion. The effects of equivalence ratio on the composition, temperature and the calorific value of produced syngas are shown in figures 3 and 4.

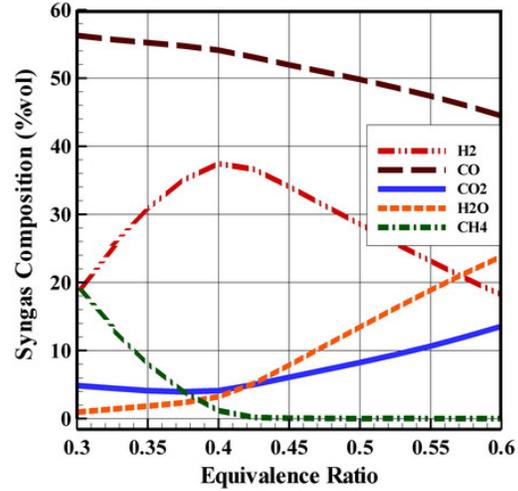


Figure 3. Effect of equivalence ratio on syngas composition

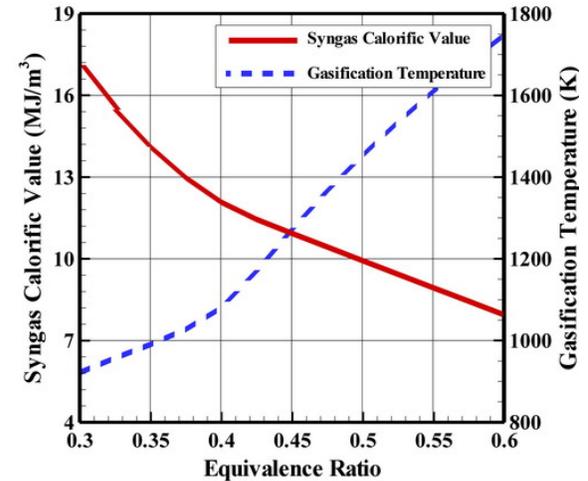


Figure 4. Effect of equivalence ratio on syngas calorific value and gasification temperature

Figure 5 shows the effect of equivalence ratio on cold gas efficiency (also known as the first law of thermodynamics efficiency) and carbon conversion efficiency. Evaluating the energy of the producer gas and that of the feedstock in the same state (reference temperature), the cold gas efficiency is written as:

$$\text{CGE} = \frac{\text{Heating value in produced syngas [MJ]}}{\text{Heating value in feed stock [MJ]}} \times 100 \quad (18)$$

and considering the amount of carbon in feedstock and produced syngas, the carbon conversion efficiency is defined as follow:

$$CCE = \left[1 - \frac{\text{Carbon in gasification residue [kmol]}}{\text{Carbon in feedstock [kmol]}} \right] \times 100 \quad (19)$$

Any increase in equivalence ratio, which leads to reduction in volume of energetic and combustible gases, reduces cold gas efficiency. At the same time, carbon conversion efficiency increases. It is due to the fact that the more oxygen available, the more carbon is combusted and, therefore, the less carbon is remained in produced syngas.

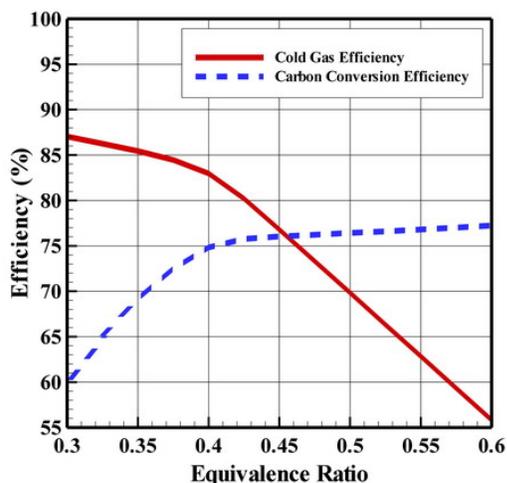


Figure 5. Effect of equivalence ratio on process efficiencies

The effects of varying gasifying agent (oxidant composition) can be seen in table 5. The results have been determined using constant operating conditions. The loss of cold gas efficiency with increasing nitrogen content of oxidant (using air as gasifying agent) is immediately noticeable. It falls off from 83.24% at 100% O_2 to 81.6% with air. The essential reason for this, and for the other effects visible in table 5, is the amount of heat required to raise the nitrogen from its preheating temperature up to the reactor outlet temperature. An approach to compensating for the heat absorption by the nitrogen might appear to be an increase in preheating temperature. Similarly the drop in useful syngas (CO and H_2) is observed as the oxygen content decreases.

Table 5. The effect of type of gasifying agent on gasification characteristics

Operating Conditions		
Gasification Pressure (atm)	10.0	
Preheating Temperature (K)	850.0	
Equivalence Ratio	0.4	
Results	Oxygen	Air
HHV (MJ/m^3)	12.0	12.3
CGE (%)	83.2	81.6
CCE (%)	75.0	73.5
Gasification Temperature (K)	1100.0	1025.0

Effect of air inlet temperature on gasification characteristics is also shown in figures 6 and 7. As the air inlet temperature increases, gasification efficiency also increases which can be used, as it was mentioned before, in order to compensate reduction in cold gas

efficiency, resulting from increasing oxidant nitrogen content. Although positive effects of increased inlet temperature can not be ignored, Klošek et al. [20] point out its limitations. The required preheat temperature of about 1200K become excessively high and unacceptable. Moreover, reduction in syngas calorific value also occurs which is not favorable.

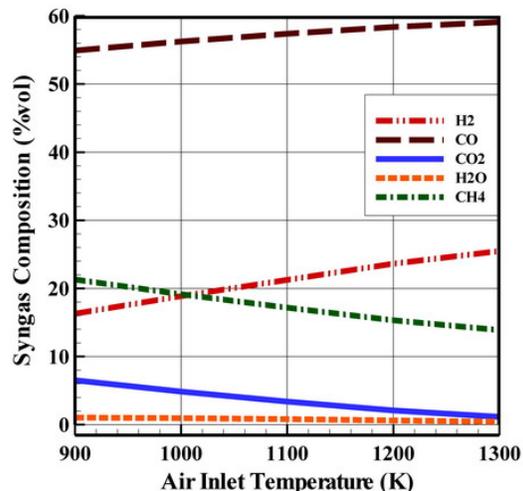


Figure 6. Effect of air inlet temperature on syngas composition

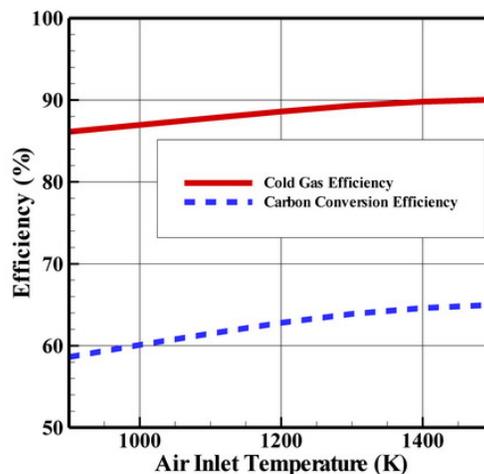


Figure 7. Effect of air inlet temperature on process efficiencies

Finally, the effect of pressure on gasification characteristics is studied. In the simulation, the pressure ranged from 1 atm to 50 atm. As it can be seen in Fig. 8, the pressure increase had negligible effects on syngas calorific value and gasification temperature. Also, an increase in CH_4 , H_2O and CO_2 contents with increasing pressure can be seen in Fig. 9. The contents of CO and H_2 , however, were reduced with pressure increase. A large increase in CH_4 content leads to an increase in syngas calorific value in spite of reduction in H_2 and CO contents. The cold gas efficiency also is reduced which in turn causes a reduction of CO and H_2 . 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 [11], the energy required to provide 100,000 m³/h syngas at 45 bar (44.4 atm) was calculated by following two methods:

- gasifying at relatively low pressure (5 bar) and compressing the gas in downstream equipment,
- 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.

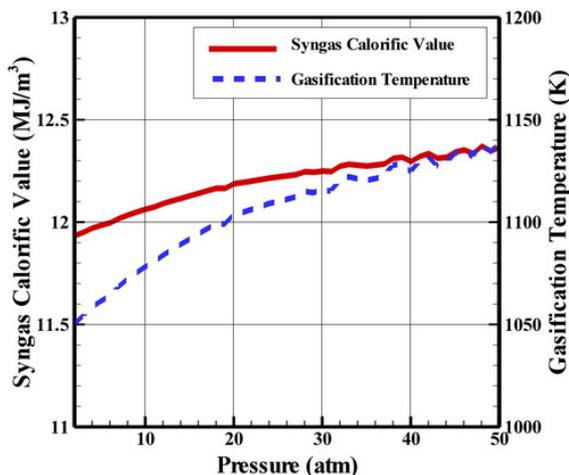


Figure 8. Effect of pressure on syngas calorific value and gasification temperature

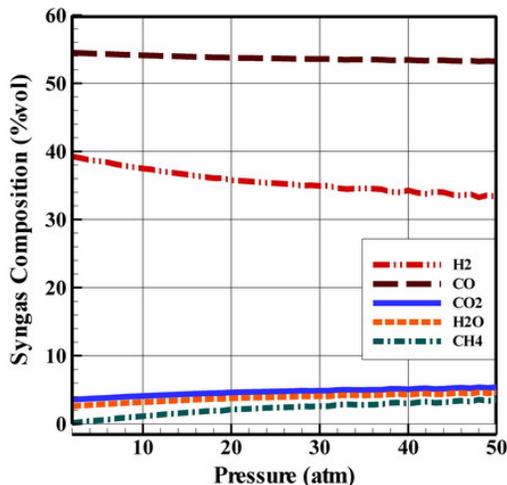


Figure 9. Effect of pressure on syngas composition

Conclusion

A numerical model for gasification of heavy fuel oils is presented. This technology, which is an alternative to combustion, results in higher efficiencies and less environmental pollutants. It is also economically preferable. The model was validated by a comparison between numerical results and those of the experiments. Increasing the oxygen ratio, which means approaching

the stoichiometric ratio or combustion, decreased the cold gas efficiency and calorific value. In other words, the increase of oxygen ratio weakens the gasification features. Air preheating can compensate for reduction in cold gas efficiency which emerges from changing gasifying agent from oxygen to air. Gasification under pressure has no noticeable effect on its characteristics; however, it is economically profitable. The developed model can be used to determine the optimum rates and ratios for a gasification process. The gasification of heavy fuel oils seems to be justifiable from whether economical, environmental or technical standpoint.

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