Research Article

Thermodynamics Analysis of Refinery Sludge Gasification in Adiabatic Updraft Gasifier

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Limited information is available about the thermodynamic evaluation for biomass gasification process using updraft gasifier. Therefore, to minimize errors, the gasification of dry refinery sludge (DRS) is carried out in an adiabatic system at atmospheric pressure under ambient air conditions. The objectives of this paper are to investigate the physical and chemical energy and exergy of product gas at different equivalent ratios (ER). It will also be used to determine whether the cold gas, exergy, and energy efficiencies of gases may be maximized by using secondary air injected to gasification zone under various ratios (0, 0.5, 1, and 1.5) at optimum ER of 0.195. From the results obtained, it is indicated that the chemical energy and exergy of producer gas are magnified by 5 and 10 times higher than their corresponding physical values, respectively. The cold gas, energy, and exergy efficiencies of DRS gasification are in the ranges of 22.9–55.5%, 43.7–72.4%, and 42.5–50.4%, respectively. Initially, all 3 efficiencies increase until they reach a maximum at the optimum ER of 0.195; thereafter, they decline with further increase in ER values. The injection of secondary air to gasification zone is also found to increase the cold gas, energy, and exergy efficiencies. A ratio of secondary air to primary air of 0.5 is found to be the optimum ratio for all 3 efficiencies to reach the maximum values.

1. Introduction

Petroleum refineries produce a lot of oily sludge and are classified as “Hazardous Waste” under Schedule Waste 2. This sludge usually contains heavy oxyhydrocarbons, traces of heavy metals such as Cd, Cu, Zn, Mn, Ni, and Pb, and water. Several conventional technologies, such as landfill and biological treatment, have been implemented to handle the waste [1]. This can lead to groundwater contamination as well as air pollution due to volatile organic chemicals, odor problem, fire hazard, and adverse health effects [2]. Combustion and incineration can help recover some of the energy and generate greenhouse gases. Instead, gasification by partial oxidation of the oily sludge can convert the hazardous material into syngas rich in H2 and CO while generating some energy as well. The gasification of a fuel involves converting the chemical energy contained in the fuel into chemical products as well as sensible energy of the produced gas. According to the first law of thermodynamics, energy can never be lost. However, according to the second law of thermodynamics energy conversion processes are accompanied by an irreversible increase in entropy, which leads to a decrease in exergy (available energy). Thus, even though the energy is conserved, the quality of energy decreases because energy is converted into a different form of energy, from which less work can be obtained [3].

Zhang et al. [4] have evaluated the biomass gasification with air in autothermal gasifiers from energy and exergy aspect. They have used two factors (ER and gasification temperature) to study the energy and exergy distribution and efficiencies. Their results indicate that the chemical energy values of product gases from biomass are 2.16–5.20 times higher as the corresponding physical energy values, while the chemical exergy values are 4.50–13.45 times as the corresponding physical exergy values. The energy and exergy efficiencies of biomass gasification are, respectively, in ranges of 52.38–77.41% and 36.5–50.19% and mainly increase and then decline when ER or gasification temperature increases.
The objectives of this paper are therefore to quantify the gasification in updraft reactor at different ER. It is also to find out whether these efficiencies could be maximized by using secondary air injected to gasification zone at various ratios. The chemical and physical energy and exergy of the producer gas are also investigated and compared with other biomass fuels.

2. Adiabatic Updraft Gasifier

The updraft gasifier unit used in this study was made from mild steel and cement with 25 mm thickness and volume of 0.16 m³. The setup of reactor rig is described by Konda et al. [8]. Figure 1 shows the exothermic and endothermic reactions in adiabatic updraft gasifier. In the drying process, the moisture in the solid fuel evaporates. The pyrolysis process separates the water vapor, organic liquids, and noncondensable gases from the char or solid carbon of the fuel. The combustion process oxidizes fuel constituents in an exothermic reaction, while the gasification process reduces them to combustible gases in an endothermic reaction. The four major gasification reactions are water-gas reaction, Boudouard reaction, shift conversion, and methanation. These are the most important reactions which could produce the syngas.

3. Thermodynamic Analysis

3.1. Mass Conversation. Mass balance or material balance is essential to validate the experimental results of the gasifier. However, to perform a mass balance for an updraft gasifier, input and output materials should be visualized. The input streams to the gasifier include DRS, dry air, and their moistures, whereas the output streams include producer gas, char, and tar.

Applying the law of conservation of mass to the gasification process yields [9]:

$$\sum M_i = \sum M_o.$$ (1)

Here the overall mass balance and its closure are calculated for DRS gasification in updraft reactor at different ER. The mass entering the updraft gasifier contains DRS and air. The products of gasification are product gas, tar, char, and ash. An overall efficiency (in terms of cold gas efficiency) of the gasification system was obtained through mass balance which could be performed for the input and output streams of the gasification process as shown in the equations below.

The mass conservation embodies

$$m_{DRS} + m_{air} = m_{DRS} + m_{tar} + m_{char} + m_{ash},$$ (2)

where $m_{DRS}$, $m_{air}$, $m_{gas}$, $m_{tar}$, $m_{char}$, and $m_{ash}$ denote the mass rates of DRS, air, product gas, tar, char, and ash, respectively.

3.2. Heat Conversation. According to energy conservation law, the corresponding energy balance of an updraft gasifier can be written as

$$E_{DRS} + E_{Air} \rightarrow E_{Gas} + E_{char} + E_{Tar} + E_{Loss},$$ (3)
The exergy balance can be written as

\[ Ex_{DRS} + Ex_{Air} + Ex_{Gas} + Ex_{Tar} + Ex_{char} + Ex_{Loss} \]

where \( Ex_{DRS} \), \( Ex_{Air} \), \( Ex_{Gas} \), \( Ex_{Tar} \), and \( Ex_{char} \) represent the exergy rates of DRS, air, product gas, char, and tar, respectively. \( Ex_{Loss} \) denotes the exergy rate lost from this system, and it includes the exergy from ash, lost heat, and irreversibility of the process.

The exergy of the product gas is comprised of two components: exergy physical \( Ex_{ph} \) and chemical exergy \( Ex_{ch} \). Neglecting the kinetic and potential exergy,

\[ Ex^o = Ex_{ph} + Ex_{ch}. \]
Here, $Ex^{ph}$ and $Ex^{ch}$ represent the physical and chemical exergy rates of the stream, respectively. The physical exergy is the maximum theoretical work obtainable as the system passes from its initial state where the temperature is the gasifying temperature and the pressure equals the gasifier pressure to the restricted dead state where the temperature is $T_0$ and the pressure is $P_0$ [12].

The physical exergy of a pure compound in a mixture can be easily calculated using enthalpy and entropy data for the given system and is given by the expression

$$Ex^{ph} = m(h - h_0) + T_0(S - S_0),$$  \hspace{1cm} (19)

where $m$ is mass flow rate of the stream in Kmol s$^{-1}$ and $S$ and $S_0$ denote the specific entropy in kJ K$^{-1}$ mol$^{-1}$ at the specified state ($P$ and $T$) and the environmental condition ($P_0 = 1$ atm and $T_0 = 298$ K), respectively. The specific entropy values of some gases are given in Table 1.

$(S - S_0)$ or $\Delta S$ is calculated from the equation below:

$$\Delta S = C_P \cdot \ln \left( \frac{T_2}{T_1} \right).$$  \hspace{1cm} (20)

The chemical exergy is the maximum theoretical useful work obtainable as the system passes from the restricted dead state to the dead state where it is in complete equilibrium with the environment [12]. The chemical exergy of the mixture $\varepsilon_{0,m}$ is determined by the composition and concentration of components in the mixture and is given by

$$\varepsilon_{0,m} = \sum_i n_i \varepsilon_{0,i} + RT_0 \sum_i n_i \ln n_i,$$  \hspace{1cm} (21)

where $\varepsilon_{0,i}$ is the standard chemical exergy of the material in kJ K$^{-1}$ mol$^{-1}$. The standard chemical exergy of a pure chemical compound is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterized by the environmental temperature $T_0$ and environmental pressure $P_0$, to the dead state, characterized not only by the same environmental conditions of temperature and pressure, but also by the concentration of reference substances in standard environment [3]. The standard chemical exergy values of some components are given in Table 1.

It should be noticed that the chemical exergy of the mixture is always lower than the sum of exergy of individual components, as the second term in the above equation is always negative.

For air the chemical exergy rate is defined as

$$Ex^{ch} = m \cdot \varepsilon_{0,j},$$  \hspace{1cm} (22)

where $m$ is stream flow rate in Kmol s$^{-1}$ and $\varepsilon_{0,j}$ (kJ Kmol$^{-1}$) is the standard chemical exergy of the component given in Table 1.

For the DRS fuel, thermodynamic properties are not available. Therefore, the statistical correlation of Szargut and Styrnylska [13] was used:

$$Ex_{DRS} = \beta \cdot LHV_{DRS} \cdot y_{DRS},$$  \hspace{1cm} (23)

Here, $\beta$ is a correlation factor and can be calculated from Szargut [14]:

$$\beta = \left( \left( 1.044 + \frac{0.016}{O} - 0.3493 \times \frac{C}{C} \right) \times \left( 1 + 0.0531 \times \frac{H}{C} + 0.0493 \times \frac{N}{C} \right) \right) \left( 1 - 0.4124 \times \frac{O}{C} \right)^{-1}.$$

$Ex_{DRS}$ is the chemical exergy of DRS. LHV and $y_{DRS}$ are the lower heating value (MJ kg$^{-1}$) and ash free fraction of DRS, respectively. C, H, O, and N are the weight fractions of carbon, hydrogen, oxygen, and nitrogen in the ultimate analysis of biomass, respectively.

The DRS considered has a higher heating value of 26.6 kJ g$^{-1}$ and lower heating value calculated from (15) is 24.99 kJ g$^{-1}$. Consider

$$y_{DRS} = 1 - y_{ash},$$  \hspace{1cm} (25)

$y_{ash}$ is the fraction of ash in the feedstock which was found to be 12.1% from the proximate analysis.

3.4. Energy and Exergy Efficiencies. To comprehensively evaluate biomass gasification, both energy and exergy efficiencies are introduced. They are defined as

$$\eta_{En} = \frac{\eta_{gas} (En_{DRS} + En_{air})}{100},$$  \hspace{1cm} (26)

$$\eta_{Ex} = \frac{Ex_{gas} (Ex_{DRS} + Ex_{air})}{100},$$  \hspace{1cm} (28)

where $\eta_{gas}$ is the energy efficiency (gas energy divided by total energy input) and $\eta_{Ex}$ is the gas exergy divided by the total input exergy.

3.5. Gasification Efficiency. Gasification efficiency is one of the important factors that determine the actual technical operation. It usually depends on the gasifier type and design as well as on the characteristics of the fuel. The gasification efficiency in this study was expressed in terms of cold gas efficiency [8, 9]:

$$CGE = \left[ \frac{Y_{gas} \left( Nm^3 kg^{-1} \right) \times HHV_{gas} \left( MJ Nm^{-1} \right)}{HHV_{fuel} \left( MJ kg^{-1} \right)} \right] \times 100,$$  \hspace{1cm} (27)

where $Y_{gas}$ is the fuel gas production, $HHV_{gas}$ is the higher heating value of the producer gas, and $HHV_{fuel}$ is the higher heating value of the DRS.

3.6. Equivalent Ratio. The equivalent ratio reflects the combined effect of the air flow rate, flow rate of DRS fuel and duration of the test. The equivalence ratio for this study was calculated by:

$$ER = \frac{m_t \times t}{M_{DRS} \times AF_{stoich}},$$  \hspace{1cm} (28)
where \( m_a \) is the air flow rate (\( m^3/h \)), \( t \) is the duration of the experiment (\( h \)), \( M_{DRS} \) is mass input of DRS fuel (kg), and \( AF_{stoch} \) is the air fuel ratio at stoichiometric conditions (7.75 \( m^3 \) of air per kg of DRS).

4. Results and Discussions

4.1. Mass and Energy Balance and Closure. The overall mass and energy balance at different equivalence ratios and their closure are computed and presented in Tables 2 and 3, respectively. From Table 2 the average mass closure is found to be 0.96, while the average energy closure (Table 3) is 0.59. Ideally, mass and closure are expected to be unity since input should be equal to output for both. However, mass closure was found to be more than 1 for some experiments which might be due to some instrumental errors as well as the residual biomass inside the gasifier, which could not be measured due to operational difficulties.

Further, the size of the gasifier contributed to these discrepancies in mass closures because of the higher probability that significant amount of refinery sludge may be retained in the gasifier after the completion of experiment. The tar production during gasification of DRS is very sticky and it is not easy to measure the total mass of tar and this introduces error in mass measurements.

Mass closure increases with ER while further increase in ER or air flow rate causes decrease in mass closure; this might be due to reduction of producer gas as the air flow increases. Further increase in ER resulted in increase in the oxidation process over the reduction process and this may reduce the amount of char production. From Table 3 a similar behavior was observed; the energy closure increases as ER increases until it reached the maximum closure of 0.75 at ER 0.195 then decreases dramatically. The lower value of energy closure might come from instrument design or construction error resulting in losing some of energy. Furthermore, the higher the ER value, the higher the \( N_2 \) (inert gas) percentages diluting the combustible gases which may lead to reducing the energy of the producer gas.

4.2. Effect of ER on Cold Gas, Energy, and Exergy Efficiencies. The influence of ER on cold gas, energy, and exergy efficiencies of product gases for dry refinery sludge gasification in adiabatic updraft gasifier is shown in Figure 2.

The maximum energy and exergy efficiencies of DRS gasification are between 72.44% and 50.38%, respectively, at ER of 0.195. Further increase in ER caused a sharp decrease in energy and exergy efficiencies. This was due to the increase of the equivalence ratio as a result of more \( O_2 \) being supplied to the gasifier, which increased the gasification temperature, hence accelerating the gasification process and improving the gas quality. Further increase in the equivalence ratio provided more \( N_2 \) with air and diluted the producer gas, which degraded the gas quality. It is also observed that the cold gas efficiency (CGE) had the same trend as that of energy and exergy; with an increase in the equivalence ratio from 0.167 to 0.21, the CGE increased from 22.97 to 55.47% and then decreased to 38.88% at maximum equivalence ratio (ER 0.24). The CGE depended upon the gas yield and the volumetric percentage of CO, \( CO_2 \), and \( CH_4 \) in the producer gas.

It is found that the cold gas and energy efficiencies are much higher than the corresponding exergy efficiencies, which is in agreement with [4]. They have found that the energy efficiencies of biomass gasification are between 52.38% (rice husk, ER = 0.25) and 77.41% (wood chip, ER = 0.38), while those of polypropylene gasification are from 54.45% (ER = 0.20) to 58.43% (ER = 0.35). The exergy efficiencies of biomass gasification are between 36.5% (rice husk, ER = 0.25) and 50.19% (wood chip, ER = 0.38). The exergy efficiencies of dry refinery sludge gasification are from 31.93% (ER = 0.24) to 50.38% (ER = 0.195). In Figure 2 when ER increases from 0.167 to 0.195, the cold gas, energy, and exergy efficiencies rise monotonously. We can foresee that these efficiencies will be reduced by the increasing \( N_2 \) which has low energy, and exergy values [4]. Resulting from the dilution of \( N_2 \), both the energy and exergy efficiencies will definitely decline when ER is high enough.

Generally speaking, the typical trend is that the cold gas, energy, and exergy efficiencies increase first and then reduce when ER increases. Hence, a proper ER should be employed to get higher efficiencies for all of them. In this work, the optimum ER for dry refinery sludge gasification in updraft reactor seems to be in 0.195.

4.3. Producer Gas Energy and Exergy Distributions. Figure 3 exhibits the energy distribution of product gases for dry refinery sludge gasification. It can be observed that the chemical energy values of product gases are much higher than the corresponding physical energy values. From the same figure it is found that the chemical energy values are 10.131 (ER = 0.195) times as the corresponding physical energy values. This relationship is mainly resulted from the fact that product gases have much higher heating values than the corresponding enthalpy values.

This result is in agreement with Zhang et al. [4], where they found that the chemical energy values are 2.16
Table 2: Effect of ER on mass balance and its closure.

| ER   | Fuel | Air | Total input (kg) | Producer gas | Char + ash (kg) | Tar | Total output (kg) | Closure |
|------|------|-----|------------------|--------------|----------------|-----|------------------|---------|
| 0.167| 15   | 18.62| 33.62           | 32.02        | 0.55           | 0.22| 32.05            | 0.98    |
| 0.19  | 15   | 23.27| 38.27           | 38.65        | 0.47           | 0.19| 35.70            | 1.02    |
| 0.195 | 15   | 27.93| 42.93           | 41.89        | 0.32           | 0.187| 39.84           | 0.99    |
| 0.21  | 15   | 32.58| 47.58           | 48.98        | 0.35           | 0.194| 40.26           | 1.04    |
| 0.22  | 15   | 37.24| 52.24           | 45.14        | 0.52           | 0.39| 35.59            | 0.88    |
| 0.24  | 15   | 41.89| 56.89           | 48.17        | 0.265          | 0.479| 38.46           | 0.86    |

Table 3: Effect of ER on energy balance and its closure.

| ER   | En DRS (kJ) | En air (kJ) | En gas (kJ) | En char (kJ) | En tar (kJ) | En closure |
|------|-------------|-------------|-------------|--------------|-------------|------------|
| 0.167| 26866       | 781.18      | 9474.71     | 4.16         | 0.94        | 0.34       |
| 0.19  | 26866       | 889.67      | 15151.79    | 4.32         | 1.19        | 0.55       |
| 0.195 | 26866       | 911.37      | 20856.65    | 0.78         | 1.04        | 0.75       |
| 0.21  | 26866       | 1009.59     | 20607.39    | 1.19         | 0.80        | 0.74       |
| 0.22  | 26866       | 1035.78     | 15914.85    | 0.81         | 0.89        | 0.57       |
| 0.24  | 26866       | 1140.32     | 15933.65    | 0.75         | 0.79        | 0.57       |

In Figure 3, the exergy values of product gases are 5.709 (ER = 0.195) times than the corresponding physical exergy values for biomass. On the whole, the physical, chemical, and total exergy values of product gases are much lower than the corresponding energy values (Figure 3). This is in agreement with the findings of other researches [4, 15, 16]. The trend of exergy value is nearly the same as that of energy. The exergy values of DRS increase first and then decline (Figure 4).

4.4. Effect of SA/PA Ratio on Cold Gas, Energy, and Exergy Efficiencies. The effect of secondary air injected to gasification zone at ER 0.195 and air flow rate of 27.93 kg/hr on cold gas, energy, and exergy efficiencies is presented in Figure 5 below. The secondary to primary air ratio is represented by (SA/PA) where SA is a secondary air flow rate measured in
Efficiency (%)

Energy
Exergy

CGE: Cold gas efficiency

$C_p$: Specific heat capacity (kJ kmol$^{-1}$K$^{-1}$)

$M$: Flow rate of stream k mol s$^{-1}$

$m_{\text{fl}}$: Mass flow rate kg hr$^{-1}$

$m_{\text{a}}$: Flow rate of air m$^3$ hr$^{-1}$

$m_{\text{f}}$: Mass flow rate of DRS kg hr$^{-1}$

$X_{\text{ash}}$: Mass fraction of ash

$\epsilon_{0,i}^*$: Standard specific exergy (kJ kmol$^{-1}$)

$a, d$: Coefficients of constant pressure specific heat capacity

$T$: Temperature (K)

$\bar{T}$: Duration time (hr or min)

$P$: Pressure (Pa)

$Z$: Height (m)

$G$: Gravitational acceleration (ms$^{-2}$)

$S$: Specific entropy (kJ kmol$^{-1}$K$^{-1}$)

$H$: Specific enthalpy (kJ kmol$^{-1}$)

$C, S$: Weight fractions in ultimate analysis

$Y$: Fuel gas production (Nm$^3$ kg$^{-1}$).

**Abbreviations**

HHV: High heating value (MJ kg$^{-1}$)

LHV: Low heating value (MJ kg$^{-1}$)

ER: Equivalent ratio

AF: Air fuel ratio.

**Greek Letters**

$\beta$: Correlation factor

$\Delta H$: Change in the system enthalpy kJ kg$^{-1}$

$\eta$: Efficiency.

**Superscripts**

Ch: Chemical

Ph: Physical

To: Total

Po: Potential

0: Standard

Ki: Kinetics.

**Subscripts**

0: Ambient condition

Air: Related to air

Uc: Related to unreacted carbon

Loss: Related to the lost

Tar: Related to tar

Gas: Related to gases

DRS: Related to dry refinery sludge

Ash: Related to ash

Stoich: Stoichiometric conditions.

**Nomenclature**

En: Energy based on one kg of DRS (kJ)

Ex: Exergy based on one kg of DRS (kJ)

From the same figure it is observed that a ratio of SA/PA = 0.5 is found to increase the cold gas, energy, and exergy efficiencies up 8.3%, 4.6%, and 3.6%, respectively, higher than their values at SA/PA = 0. It can be recommended that using secondary air at optimum ER for gasification process is found to increase the gasification energy and exergy efficiencies in adiabatic updraft gasifier.

**5. Conclusions**

Based on the gasification of dry refinery sludge in updraft reactor, the chemical energies of producer gases are 6.8–10.1 times higher while the chemical exergies are 2.3–5.7 times higher than the corresponding physical values. DRS has higher carbon and hydrogen content as indicated in the ultimate analysis. This therefore generates higher gaseous energy and exergy values. The cold gas, energy, and exergy efficiencies of DRS gasification are in the ranges of 22.9–55.5%, 43.7–72.4%, and 31.92–50.4%, respectively. During the process it increases initially till it reaches the maximum at the optimum ER of 0.195 and thereafter declines with further increase in ER value. The increase in ER results in more $O_2$ being supplied to the gasifier, increasing oxidation process which further contributes to increase in gasification temperature. This causes a decline in the gas quality, energy, and exergy. Further, increase in the equivalence ratio injects more $N_2$ with air and dilutes the producer gas, which also degrades the gas quality. When an optimum ratio of secondary air to primary air of 0.5 is injected at the gasification zone it was found that the energy values of product gases are much higher than the corresponding exergy values, which results in higher energy efficiencies.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.
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