25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COBEM2019-0382
CHARACTERIZATION OF OILY SLUDGE AND COMPUTATIONAL SIMULATION OF ITS GASIFICATION

York Castillo Santiago
Diego Mauricio Yepes Maya
Osvaldo José Venturini
Electo Eduardo Silva Lora
Excellence Group in Thermal Power and Distributed Generation-NEST, Institute of Mechanical Engineering, Federal University of Itajubá-UNIFEI, Av. BPS 1303, Itajubá, MG, Brazil
e-mail: yorkcastillos@gmail.com, diegoyepes@unifei.edu.br, silva.electo52@gmail.com, osvaldo@unifei.edu.br

Marcelo Ricardo Queiroz Medeiros
Leopoldo Américo Miguez de Mello Research Center (CENPES), Petrobras, Av.Horácio Macedo 950, Rio de Janeiro, Brazil.
e-mail: marcelorqm@petrobras.com.br

Abstract. *Thermochemical conversion of oily sludge (OS) from refineries was investigated to evaluate syngas production. A preliminary characterization of OS indicated that it has a Higher Heating Value (HHV) of 42.6 MJ/kg, a large concentration of Chromium and Cobalt, Quartz and Cristobalite between its crystalline phases, as well as a viscosity of 8550 mPa·s at a temperature of 80.5 °C. Simulation of an equilibrium model with air as gasifying agent using Aspen Plus 11.0® software was accomplished to analyze the effects of the gasifying agent quantity on OS gasification parameters. The results indicated that using an equivalence ratio (ER) of 0.30 and humidity of 10%, the Low Heating Value (LHV) of Syngas is 5.1 MJ/Nm^3. The OS gasification process could become an added value technological alternative for oily waste treatment from the crude oil refining.*

Keywords: *oily sludge, gasification, thermal treatment, petroleum waste*

1. INTRODUCTION

In general, OS (Fig. 1) is a recalcitrant residue with a pH in the range of 6.5 to 7.5, characterized as a stable emulsion of water, solids, petroleum hydrocarbons (PHCs) and metals (Mazlova and Meshcheryakov, 1999). Due to the existence of high concentrations of PHCs, OS has been recognized as a hazardous waste that threatens the environment and human health (Martínez González et al., 2018).

Figure 1. Typical appearance sample of OS

According to the report released by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP, 2018), in 2017 the national oil production reached 2.6 million barrels a day, leaving Brazil in the ninth place in the world ranking of oil producers. Considering that the petrochemical industry generates a considerable amount of OS (almost 2.0 kg per each ton of refined crude oil produced) with a density of 870 kg/m^3 (Xu et al., 2009), in Brazil 719 tons of OS are produced per day.

A variety of physical-chemical, biological and thermal methods for the treatment of OS have been developed. However, the efficiency of chemical and biological treatment systems for OS is affected by the formation of stable oil-in-water emulsions, which leads to an increase in investment and operational cost compared to the thermal treatment (Hu et al., 2013). Thermal processes, such as pyrolysis, gasification, and combustion, have been proposed for the treatment of OS since they can destroy the organic fractions of the sludge and convert the inorganic fractions to stable ash or slag, and so are considered the most promising methods for the treatment of OS (Gomez et al., 2009). Gasification is a technology that reduces the volume of waste, removes toxic organic compounds and fixes heavy metals into the residual solids, while converting a carbon-containing material into a combustible gas composed primarily of carbon monoxide, hydrogen, and methane, which can be used as fuel to generate electricity and heat (Midilli et al., 2001).

The gasification process depends on a bunch of complex chemical reactions, including partial oxidation, conversion of tar and lower hydrocarbons, among others. Therefore, this complicated process, coupled with the sensitivity of the product distribution to the rate of heating and residence time in the reactor, as well as its dependence on temperature and pressure, requires the development of mathematical models to evaluate its performance (Puig-Arnavat et al., 2010). A widely used model for gasification is the thermodynamic equilibrium model, which provides the maximum possible yield of the desired products from a reagent system. This considers the reaction alone, regardless of the gasifier's geometry (Dutta et al., 2014). The thermodynamic equilibrium calculations are independent of the gasifier configuration and, therefore, it is convenient to study the influence of the process parameters. The equilibrium models can be divided into two categories according to the method used to calculate the chemical equilibrium: (i) stoichiometric models and (ii) non-stoichiometric models. In stoichiometric models the equilibrium is determined by using equilibrium constants for each reaction involved in the process, while in non-stoichiometric models, it is determined by the minimization of Gibbs free energy (Gambarotta et al., 2018).

Among the works of oil gasification models it is possible to find the one developed by Martínez González et al. (2019), that considered a kinetic model of simulation with air/steam mixtures using Aspen Hysys 8.6® software to evaluate the effect of gasification agents on OS gasification parameters, using energetic and exergetic analysis. The authors used the kinetic parameters of the compounds obtained in the saturates, aromatic, resin and asphaltene analysis, and found a decreasing trend in the LHV of the syngas produced when the ER and steam/OS ratio (SOS) was increased, reaching values between 5 and 10 MJ / Nm^3 for ER> 0.30 and SOS between 0.5 and 1.5, while the yield of syngas may range from 2.0 to 5.0 Nm^3 H_2/ kg OS with an H_2 content of about 25% (mol%) under the same conditions. When considering an integrated gasification system for energy generation and exergetic balance, the exergy destruction was increased almost three-fold in relation to syngas production from the gasification process, resulting in 64.4% of total exergy integrated plant.

Yue et al. (2016) elaborated a kinetic model of heavy oil gasification in the presence of CaO that can predict syngas yield, tar concentration, and performance parameters. The results showed that CaO plays an important role in a significant reduction of CO_2 during the process and that there is an optimum condition for the yield of tar, which can be calculated through a parametric analysis. The authors also found that the CaO/fuel relation has a positive impact on tar cracking, although it is not significant. On the other hand, Ghassemi et al. (2015) conducted a comprehensive study on extra-heavy oil gasification using the Gibbs free energy minimization approach. The model developed can predict the concentration components produced and the performance parameters of gasification under actual operating conditions. The authors found that an increase in the ER leads to a considerable decrease in the higher calorific value of the syngas and the efficiency of the cold gas, while the efficiency of the char conversion increases. The study also illustrated that increasing the pressure from 10 to 50 atm has no significant effect on the increase in the higher calorific value of the dry gas.

Based on the previous discussion, the present work aims to determine the energetic potential of the syngas produced by the gasification of OS, using Aspen Plus 11.0® software, based on the characterization performed on OS sample.

2. MATERIALS AND METHODS

Initially, it was studied the possibility of energy conversion of OS, a residue resulting from the processing of crude oil that until now has not a clearly defined use and which, in addition, poses a risk to the environment. Therefore, bibliographical and documentary sources were consulted in search of information that would make feasible the proposal to use OS for energy purposes, where the gasification was selected. Afterward, the physicochemical characterization of OS was done in the laboratories of the NEST research group of the Federal University of Itajubá, and the data obtained were used in the simulation of the gasification process. From the simulation, the main variables that influence the performance of OS gasification were established to obtain a syngas rich in hydrogen and carbon monoxide.

The following four subsystems were defined for the simulation of OS gasification process: (i) drying, (ii) pyrolysis, (iii) oxidation/reduction and (iv) syngas treatment. The simulation scheme is presented in Fig. 2, where three reactors must be used because in Aspen Plus® the stoichiometric reactions and equilibrium cannot be carried out in the same reactor.

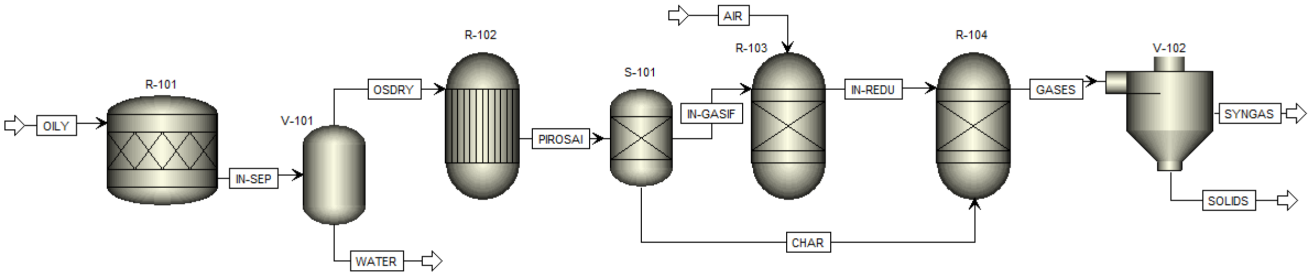

Figure 2. Simulation of OS gasification.

The block used for the drying stage of the raw material (OILY) is a stoichiometric reactor (R-101), which allows the use of several reactions with the molar extent of conversion or fractional conversion of a component. The separator block (V-101) is responsible for separating the dry material (OSDRY) from the water vapour (WATER).

For the pyrolysis stage, a yield reactor block (R-102) was used, which is useful when the distribution of products was known while the reaction stoichiometry and kinetics were unknown. This reactor was used to simulate the decomposition of the dried OS into its elemental components, including C, H_2, O_2, N_2, S, ash, and moisture. This function was performed through a programed FORTRAN statement with the OS ultimate analysis data. The R-102 has as input the OSDRY flow of the previous block and outputs the IN-GASIF flow which is formed by light gases and char. Unconverted char is separated into block S-101 and sent to the GIBBS reactor (R-104).

The block used to simulate the oxidation process is a Gibbs Reactor (R-103), which is responsible for estimating the composition of the outgoing gases when the process reaches chemical equilibrium. This block receives the IN-GASIF flow from block S-101 and once in R-103, airflow under atmospheric conditions is injected into the reactor. The gasifying agent selected for this study was air. The reduction/char gasification zone is simulated in R-104, which receives the products of the oxidation zone (IN-REDU) and the CHAR stream, resulting in the GASES current corresponding to the syngas.

Since the output stream, GASES is a mixture of gases and solids (ashes), it is necessary to separate these compounds into two independent streams to isolate the syngas that will be used in different applications such as power and heat generation. The separation was simulated by the Split Separator block (V-102), the resulting SYNGAS are formed by N_2, H_2, CH_4, CO, and CO_2, while the SOLIDS are simply ashes.

In order to analyze the decomposition of the compounds present in OS, some chemical reactions of catalytic reforming with steam and partial oxidation were considered for the defined zones for OS gasification. All these reactions are presented in Tab. 1.

Table 1. Chemical reactions considered in the gasification

Chemical reaction	Reaction Heat (kJ/mol)	Reaction name	Zone
OS $\rightarrow$ volatiles (H_2, CO, CO_2, H_2O, CH_4) + Char	-	Pyrolysis	Pyrolysis
$H_2 + ½O_2 \rightarrow H_2O$	-242	H_2 oxidation	Oxidation
$CO + ½O_2 \rightarrow CO_2$	-238	CO oxidation	Oxidation
$C + ½O_2 \rightarrow CO$	-111	Char partial oxidation	Oxidation
$C + O_2 \rightarrow CO_2$	-394	Char total oxidation	Oxidation
$C + CO_2 \leftrightarrow 2CO$	+172	Boudouard	Reduction
$CO + H_2O \leftrightarrow CO_2 + H_2$	-41	Water Gas Shift	Reduction
$C + H_2O \leftrightarrow CO + H_2$	+131	Water Gas	Reduction
$C + 2H_2 \leftrightarrow CH_4$	-75	Methanation	Reduction
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206	Steam methane reforming	Reduction

Source: adapted from Susastriawan et al. (2017) and Han et al. (2017)

3. RESULTS AND DISCUSSION

The OS samples (vacuum residue) were obtained from a distillation tower, classified according to the industry as a clean waste because it has low solids particles content and still has energy content with the capacity to generate combustible products with high energy value (Jafarinejad, 2016). Aspen Plus® has in its database conventional and unconventional compounds, since OS is in the category of non-conventional because it does not have an exact chemical formula, it is necessary to provide the physical-chemical characterization of this residue from the petroleum industry.

3.1 Analysis of heavy metals by atomic absorption spectroscopy

In order to perform the analysis of heavy metals, digestion was made for each one of the samples of OS in order to make an extraction of the chemical elements present. For this procedure, 0.5 grams of the sample mixed with 10 mL of nitric acid was used. Subsequently, samples were digested in a microwave oven using two stages, the first for 4.5 minutes at 170 ° C and the second for 5.5 minutes at 180 ° C (EPA, 2007). Finally, the samples were filtered on Whatman 42 paper and taken for quantitative analysis by scanning the atomic emission spectrometer. The results with a relative standard deviation of ± 0.05% are presented in Tab. 2.

Table 2. Concentration of metals present in OS

Element	mg/L	mg/kg
Zinc	0.4795	12.467
Nickel	0.602	15.652
Copper	0.219	5.694
Cobalt	2.586	67.236
Lead	0.590	15.340
Chrome	4.939	128.414

3.2 Viscosity

OS samples used in the tests are in a solid state at room temperature, so it was necessary to preheat the samples for 10 minutes at 85 °C since at this temperature the sample can flow. Figure 3 shows the viscosity curve that was obtained, in which it can be observed that for a range between 81.8 ° C and 80.5 ° C the viscosity values are between 4500 and 8500 mPa·s, respectively. The method used for the calculation of viscosity was based on (ASTM, 2015).

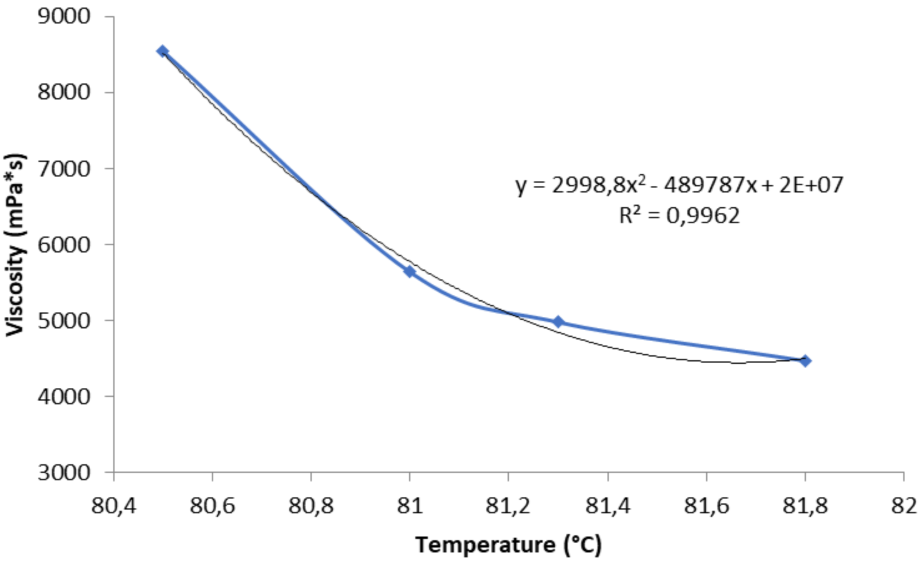

Figure 3. Viscosity curve of OS

3.3 Ultimate analysis

Elemental analysis was performed using the CHNS method based on (ASTM, 2008), where the percent concentrations of C, H, N, and S are quantified, with O_2 being determined by difference. Three replicates were performed for the studied sample and the results with a relative standard deviation of ± 0.2% can be observed in Tab. 3. For the model, the average value presented in Tab. 3 was used.

Table 3. Elementary composition of OS.

	C (%)	H (%)	N (%)	S (%)	O (%)
Test 1	82.07	10.21	0	5.21	2.51
Test 2	81.23	10.25	0	5.18	3.34
Test 3	82.04	10.35	0	5.28	2.33
Average value	81.78	10.27	0	5.22	2.73

3.4 Proximate analysis

For the immediate analysis, tests were performed with an atmosphere of N_2, using three different heating ramps to determine the immediate composition based on the method of (ASTM, 2013). Three replicates were used for each heating ramp of 5, 10 and 20 °C/min. The results of the immediate composition considering each heating ramp with a relative standard deviation of ± 0.02%, as well as the average composition, which will be used in the model are presented in Tab. 4. For the model, the average value presented in Tab. 4 was used.

Table 4. Immediate composition of OS.

Heating ramp	Moisture (%)	Volatile (%)	Ash (%)	Fixed carbon (%)
5°C/min	0.003	85.433	0.210	14.357
10°C/min	0.037	86.013	0.123	14.213
20°C/min	0.030	86.353	0.347	13.273
Average value	0.023	85.933	0.227	13.948

3.5 X-ray diffraction

The analysis was performed through the powder method, using an X-ray diffractometer with a position-sensitive detector (Knapp et al., 2004). Fig. 4 shows the diffractogram (red color) obtained for OS, where the diffraction lines corresponding to the identified phases, blue for quartz and purple for cristobalite

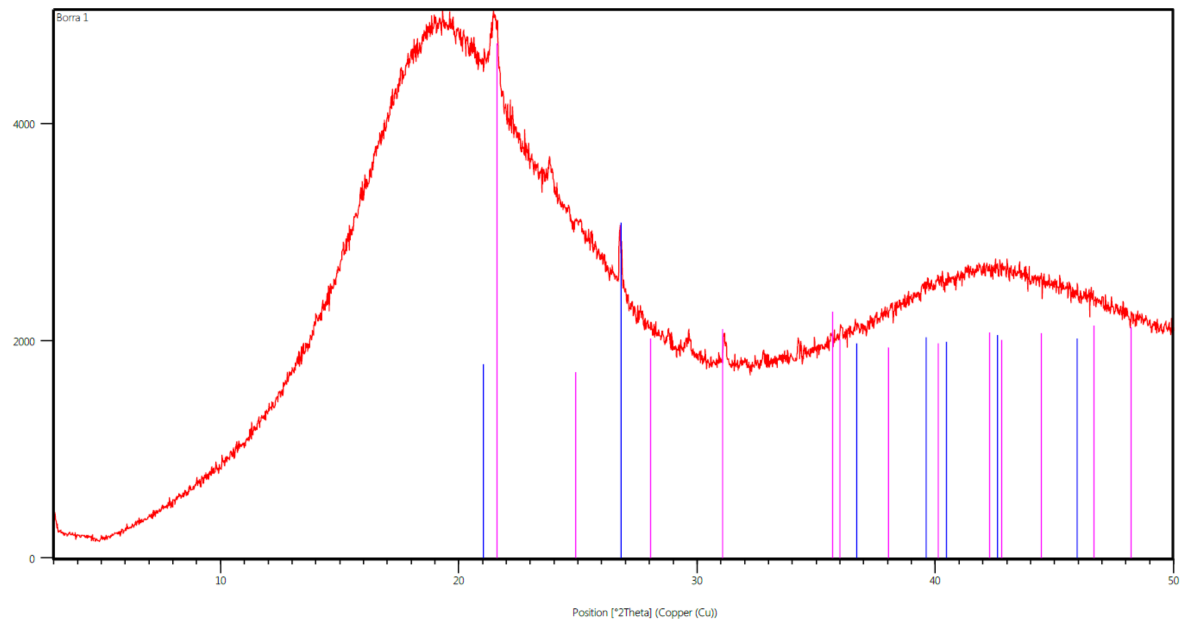

Figure 4. Diffractogram for OS

3.6 Result obtained from the model developed

The ER is an important parameter in the gasification of OS, and it is related to the amount of synthesis gas produced. The model using data from OS characterization showed that the yield of syngas increases as the ER increases and the moisture decreases, as shown in Fig. 5. It can be observed that with an ER of 0.3 and moisture of 10%, the highest production of syngas (3.7 Nm^3/kg OS) was obtained.

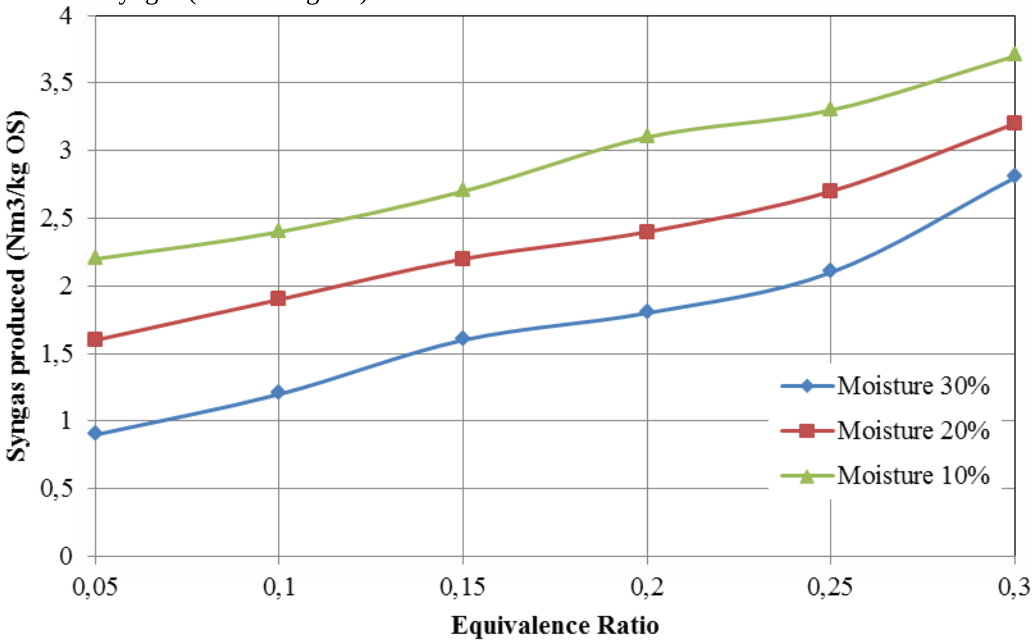

Figure 5. Influence of moisture and equivalence ratio (ER) on the production of syngas.

Figure 6 shows the effect of the OS moisture content on the concentration of CO, CH_4, and H_2 in the syngas obtained, for an ER of 0.3.

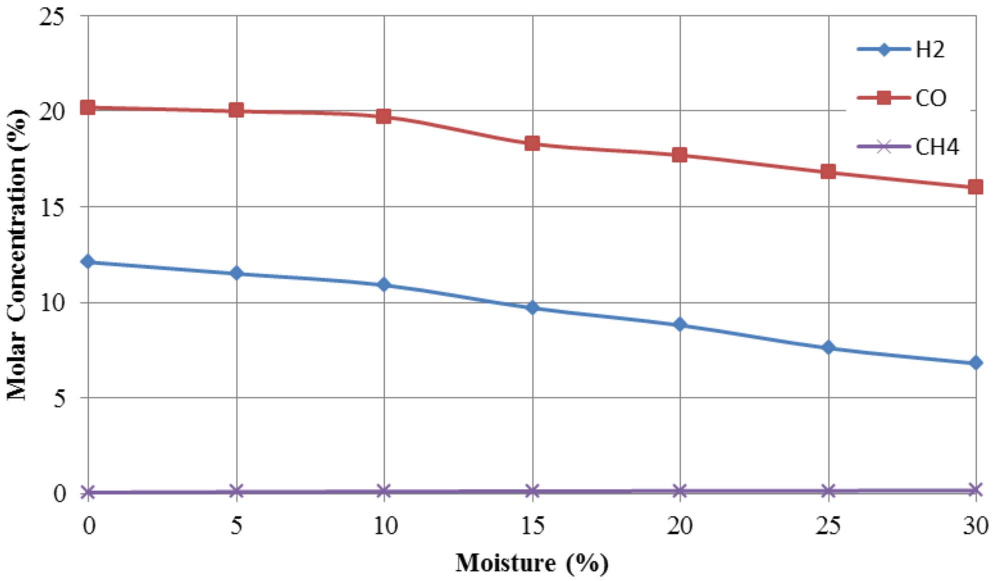

Figure 6. Analysis of the concentration of the compounds present in the syngas as a function of the humidity of OS

The molar concentration of CO and H_2 decrease, whereas the CH_4 variation is practically null, this is because higher water content leads to lower molar concentrations in the syngas. For variations of moisture between 0% and 10%, no significant effects on the composition of the gas are observed, despite the increase in the energy cost that would imply drying the OS to reduce its moisture content to less than 10% in the process.

The syngas LHV is estimated from the concentration of the gas components using Eq. (1), modified by Han et al. (2017). This parameter, together with the rate of gas generation, can be used to estimate the energy potential of syngas from OS.

$$LHV = y_{H_2} LHV_{H_2} + y_{CO} LHV_{CO} + y_{CH_4} LHV_{CH_4} \tag{1}$$

Where y represents the mole fraction of the compound. The LHV of H_2, CO and CH_4 are 11.2 MJ/Nm^3, 13.1 MJ/Nm^3, and 37.1 MJ/Nm^3, respectively.

The maximum value obtained for the LHV of the syngas obtained was 5.1 MJ/Nm^3, and it occurs at the lowest moisture content (10%), where higher values of molar concentrations of H_2 and CO are obtained according to the data shown in Fig. 6.

4. Conclusions

This study considers the possibility of thermochemical conversion of OS from refined crude oil via gasification. In relation to the behavior of the OS analyzed, it was observed that it has a high HHV and at room temperature, it is in solid state, while at temperatures in the range of 80.5 °C to 81.5 °C it can flow, because with these temperatures has viscosities between 4500 and 8500 mPa·s. In the case of analysis of metals, OS presented higher concentrations of chromium (128.414 mg/kg) 20 times greater compared to copper (5.694 mg/kg). According to the simulation results, increases of ER lead to syngas yield increases, since for an ER of 0.05 the syngas yield was 2.2 Nm^3/kg OS while for an ER of 0.3 it was 3.7 Nm^3/kg OS, which favors the decomposition and reform of the hydrocarbons present in the OS and therefore, a greater amount of syngas per OS mass unit is produced. On the other hand, the maximum LHV of the syngas was 5.1 MJ/Nm^3, obtained with a OS humidity of 10%, since in this condition it is possible to obtain higher concentrations of H_2 and CO. Gasification represents a promising technological alternative for the management and treatment of OS, since it considerably reduces the environmental impact of traditional methods of treatment of this residue and, at the same time, brings a possible economic gain with the possibility of generating electricity.

5. ACKNOWLEDGMENTS

The authors wish to express their thanks to the Research Support Foundation of the state of Minas Gerais (FAPEMIG), the National Council for Scientific and Technological Development (CNPq), the Committee for Coordination of Improvement in Higher Education (CAPES), and to PETROBRAS for funding through grants and awards.

6. REFERENCES

ANP, 2018. Anuário estatístico brasileiro do petróleo, gás natural e biocombustíveis. Rio de Janeiro.

ASTM, 2015. ASTM D5133-15, Standard Test Method for Low Temperature, Low Shear Rate, Viscosity/Temperature Dependence of Lubricating Oils Using a Temperature-Scanning Technique. West Conshohocken, PA.

ASTM, 2013. ASTM D3172-13, Standard Practice for Proximate Analysis of Coal and Coke. West Conshohocken, PA.

ASTM, 2008. ASTM D5373 - 08, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal. West Conshohocken, PA.

Dutta, P.P., Pandey, V., Das, A.R., Sen, S., Baruah, D.C., 2014. Down draft gasification modelling and experimentation of some indigenous biomass for thermal applications. Energy Procedia 54, 21–34. https://doi.org/10.1016/j.egypro.2014.07.246

EPA, 2007. Microwave assisted acid digestion of sediments, sludges, soils and oils [WWW Document]. URL https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf (accessed 3.12.19).

Gambarotta, A., Morini, M., Zubani, A., 2018. A non-stoichiometric equilibrium model for the simulation of the biomass gasification process. Appl. Energy 227, 119–127. https://doi.org/https://doi.org/10.1016/j.apenergy.2017.07.135

Ghassemi, H., Beheshti, S.M., Shahsavan-Markadeh, R., 2015. Mathematical modeling of extra-heavy oil gasification at different fuel water contents. Fuel 162, 258–263. https://doi.org/10.1016/j.fuel.2015.09.018

Gomez, E., Rani, D.A., Cheeseman, C.R., Deegan, D., Wise, M., Boccaccini, A.R., 2009. Thermal plasma technology for the treatment of wastes: A critical review. J. Hazard. Mater. 161, 614–626. https://doi.org/10.1016/j.jhazmat.2008.04.017

Han, J., Liang, Y., Hu, J., Qin, L., Street, J., Lu, Y., Yu, F., 2017. Modeling downdraft biomass gasification process by restricting chemical reaction equilibrium with Aspen Plus. Energy Convers. Manag. 153, 641–648. https://doi.org/https://doi.org/10.1016/j.enconman.2017.10.030

Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: A review. J. Hazard. Mater. 261, 470–490. https://doi.org/10.1016/J.JHAZMAT.2013.07.069

Jafarinejad, S., 2016. Odours emission and control in the petroleum refinery: a review. Curr Sci Perspect 2, 78–82.

Knapp, M., Joco, V., Baehtz, C., Brecht, H.H., Berghaeuser, A., Ehrenberg, H., von Seggern, H., Fuess, H., 2004. Position-sensitive detector system OBI for High Resolution X-Ray Powder Diffraction using on-site readable image plates. Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip. 521, 565–570. https://doi.org/https://doi.org/10.1016/j.nima.2003.10.100

Martínez González, A., Silva Lora, E.E., Escobar Palacio, J.C., 2019. Syngas production from oil sludge gasification and its potential use in power generation systems: An energy and exergy analysis. Energy 169, 1175–1190. https://doi.org/https://doi.org/10.1016/j.energy.2018.11.087

Martínez González, A., Silva Lora, E.E., Escobar Palacio, J.C., Almazán del Olmo, O.A., 2018. Hydrogen production from oil sludge gasification/biomass mixtures and potential use in hydrotreatment processes. Int. J. Hydrogen Energy 43, 7808–7822. https://doi.org/10.1016/j.ijhydene.2018.03.025

Mazlova, E.A., Meshcheryakov, S. V, 1999. Ecological characteristics of oil sludges. Chem. Technol. Fuels Oils 35, 49–53. https://doi.org/10.1007/BF02694263

Midilli, A., Dogru, M., Howarth, C.R., Ling, M.J., Ayhan, T., 2001. Combustible gas production from sewage sludge with a downdraft gasifier. Energy Convers. Manag. 42, 157–172. https://doi.org/10.1016/S0196-8904(00)00053-4

Puig-Arnavat, M., Bruno, J.C., Coronas, A., 2010. Review and analysis of biomass gasification models. Renew. Sustain. Energy Rev. 14, 2841–2851. https://doi.org/https://doi.org/10.1016/j.rser.2010.07.030

Susastriawan, A.A.P., Saptoadi, H., Purnomo, 2017. Small-scale downdraft gasifiers for biomass gasification: A review. Renew. Sustain. Energy Rev. 76, 989–1003. https://doi.org/https://doi.org/10.1016/j.rser.2017.03.112

Xu, N., Wang, W., Han, P., Lu, X., 2009. Effects of ultrasound on oily sludge deoiling. J. Hazard. Mater. 171, 914–917. https://doi.org/10.1016/j.jhazmat.2009.06.091

Yue, X.-G., Esfahani, M.J., Akbai, H., Foroughi, A., 2016. A kinetic model for gasification of heavy oil with in situ CO<inf>2</inf> capture. Pet. Sci. Technol. 34, 1833–1836. https://doi.org/10.1080/10916466.2016.1227837

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.