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Hydrogen production from oil sludge gasification/biomass mixtures and potential use in hydrotreatment processes

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ABSTRACT

Gasification of oil sludge (OS) from crude oil refinery and biomass was investigated to evaluate hydrogen production and its potential use in diesel oil hydrodesulphurization process. Gasification process was studied by Aspen Hysys® tools, considering different kinetic model for main OS compounds. Air and superheated steam mixtures as gasifying agents were simulated. Gasification parameters like: temperature, syngas chemical composition and gas yield were evaluated. Results showed OS thermal conversion needs a working temperature above 1300 °C to ensure a high conversion (>90%) of OS compounds. Thermal energy requirement for gasification was estimated between 0.80 and 1.25 kWh/kg OS, considering equivalence air (ER) and steam/oil sludge (SOS) ratio between 0.25-0.37 and 0.2–1.5 kg steam/kg OS, respectively. The gas yield was 2.28 Nm^3/kg OS, with a H_2 content close to 25 mol%, for a H_2 potential production about 1.84 Nm^3 H_2/kg OS; nevertheless, when OS and biomass mixtures are used, hydrogen production increases to 3.51 Nm^3 H_2/kg OS, meaning 37% of H_2 (from natural gas) required for diesel oil hydrodesulphurization could be replaced, becoming an added value technological alternative for OS waste conversion as a source of H_2, inducing a considerable reduction of greenhouse gases and non-renewables resources.

Introduction

According to the OPEC report, global refinery capacity for crude oil is above 90 mb/d (4313 million tons/year, based on crude oil WTI at 39.6 API) [1]. This industry generated a considerable amount of oil sludge (OS), producing around 1.0 ton of this residue for every 500 tons of crude oil processed (0.2 wt%) [2], where United States and China are the largest producers, with an annual production of O nearly 4.5 and 3.0 million tons, respectively [3,4], whereas, the amount OS produced by the petrochemical industry in Brazil was estimated in 0.23 tons per year. In these sense, in coming years, a global production of OS between 8.6 and 43 million tons/year is expected considering a OS production yield around 0.2 and 1.0 wt% of oil processed, respectively.

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Abbreviations

BOS	Biomass-to-oil sludge ratio
BTX	Benzene Toluene Xylene
ER	Equivalence ratio
LHV	Lower heating value
HHV	Higher heating value
HDT	Hydro-desulfurization technology
HSD	High sulfur diesel
OS	Oil Sludge
PAH	Polycyclic aromatic hydrocarbon
SARA	Saturated aromatic resins asphaltenes
SOS	Steam-to-oil sludge ratio
SS	Steam-to-syngas ratio
TPH	Total petroleum hydrocarbon
WGS	Water–gas shift
mb/d	Millions of barrels per day
r_i	Chemical reaction rater (mol/m^3-s)
A_i	Pre-exponential factor from Arrhenius's equation (1/s)
E_{ai}	Activation energy (kJ/kmol)
R	Ideal gas constant (8.3145 kJ/kmol-K)
T	Absolute temperature (K)
$[C_xH_y]$	Molar concentration of hydrocarbon (mol/m^3)
$[H_2]$	Molar concentration of hydrogen (mol/m^3)
$[O_2]$	Molar concentration of oxygen (mol/m^3)
$[H_2O]$	Molar concentration of water (mol/m^3)
$[CO_2]$	Molar concentration of carbon dioxide (kmol/m^3)
$[C_{12}H_8S]$	Mass concentration of hydrocarbon dibenzothiophene (ppm)
α	Order of chemical reaction with respect to hydrocarbon (-)
β	Order of chemical reaction with respect to hydrogen (-)
γ	Order of chemical reaction with respect to oxygen (-)
δ	Order of chemical reaction with respect to water (-)
ε	Order of chemical reaction with respect to carbon dioxide (-)
a	Index of temperature intensity in chemical kinetic

Oil sludge is considered a recalcitrant residue, consisting mainly of a complex mixture of water, solids, heavy hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and heavy metals [5,6]. Its pH value can range from 6.5 to 7.5 and its chemical composition depends on: oil origin, oil process scheme, equipment and reagents used in refining process. OS total petroleum hydrocarbon (TPH) content may range from 5 to 86.2 wt%, whereas water and solids content will range from 30 to 85 wt% and 5–46 wt%, respectively [7]. OS organic compounds content can generally be classified into four fractions: aliphatic, aromatic, NSO compounds (Nitrogen, Sulfur and Oxygen) and asphaltenes [8]. In this way, the most common compounds are: alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, and various PAHs, among them: phenanthrene, anthracene, chrysene, benzofluorene, and pyrene [3]. Presence of asphaltenes and resins along with free water can be responsible of oil-water emulsion stability, since these components contain hydrophilic fractions [9,5].

In recent years, management and final disposal of OS generated during oil refining process has received increasing attention due to its high concentration of PAHs and heavy metals, being recognized as a hazardous waste in many countries, in such a way that inadequate disposal or insufficient treatment can pose serious threats to environment stability and human health [10,8]. A variety of physicochemical, biological and thermal methods for OS treatment have been recently developed, such as: centrifugation, solidification/stabilization, solvent extraction, ultrasonic treatment, incineration, pyrolysis [11–13], and in some literature reporting use of microbial and biodegradable materials [3,14]. However, the efficiency of chemical and biological OS treatment systems is affected by the formation of water-oil stable emulsion, which leads an increase in investment and operational cost in comparison with thermal treatment [15]. So, thermal processes like pyrolysis and gasification have become promising methods for OS treatment, where significant production of fuel gases and liquids with high hydrocarbon content (C_xH_y) are expected with physic-chemical characteristics comparable to low grade petroleum distillates [16–18].

Shuo et al. [19] accomplished OS pyrolysis with oil sludge ash additive and noted that oily products quality was improved by Al_2O_3, Fe_2O_3 addition. Huang et al. [20] proposed catalytic pyrolysis in two stages for treatment of different OS types, showing that for catalytic temperatures higher than 1000 °C the hydrogen production rate can range from 0.11 Nm^3/kg OS to 0.28 Nm^3/kg OS, while temperatures lower than 1000 °C favor the production of CH_4 and CO. Moltó et al. [21] studied OS pyrolysis/gasification from different sources of a crude oil refinery. Influence of heating rate, oxygen presence and residence time over syngas composition was tested, finding for a heating rate of 4 K/s the highest H_2/CO ratio. Nevertheless, for higher heating rates of about 10 K/s a reduction in H_2 composition was observed, while CH_4 and CO_2 syngas contents were increased. Pánek et al. [22] evaluated OS pyrolysis by thermo-gravimetry in a laboratory-scale reactor using calcium oxide as an additive, which limits char formation (solid coal) to less than 2 wt% and promotes large amount of oil rich on aliphatic compounds with a Higher Heating Value (HHV) of about 42 MJ/kg and low sulfur content.

Gasification is considered a clean technology for energy conversion with minimum environmental impact using biomass and solid wastes as feedstock. Although OS gasification is not common, this technology is used to obtain a producer gas rich in H_2, CO, CH_4 and (C_xH_y) [23]. However, gas composition depends on raw material, operating conditions and gasifier design, as well as on gasifying agent (air, vapor, oxygen or mixtures between them) [24,25]. Production of hydrogen-enriched syngas from renewable biomass or organic wastes through gasification process has been intensively explored because of its low operation cost and high possibility for commercialization [26,27]. Many scientific works have been dealing with enhancing hydrogen yield from various wastes. Cao et al. [28] tested sugarcane bagasse

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