GASIFICATION OF GLYCEROL INTO SYNGAS (H₂+CO) BY THERMAL AIR PLASMA

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REFERENCE NO	ABSTRACT
GASF-02	Increasing global biodiesel production causes excess of crude glycerol. Nowadays, ongoing research are focused on the findings of the most appropriate way for the conversion of glycerol into beneficial products such as syngas, hydrogen. Consequently, the purpose of this study was to investigate air plasma suitability to decompose crude glycerol into syngas using DC thermal arc plasma torch operating at atmospheric pressure. The gasification of glycerol was performed at various air flow rates and plasma torch power. The gasification system was quantified in terms of the carbon conversion efficiency, cold gas efficiency, energy efficiency, specific energy requirement. It was found that the syngas with a lower calorific value was produced during the gasification of crude glycerol. Also, it was determined that the gasification effectiveness depends on the $Air/C_3H_8O_3$ ratio and the power of the plasma torch. This study specifies that thermal air plasma is suitable for the gasification of crude glycerol.
Keywords: glycerol, gasification, thermal plasma, syngas	

1. INTRODUCTION

Depleting fossil fuel reserves and on-going climate change encouraged search for alternative, environmentally benign energy resources. In this regard, biodiesel attracted the attention as sustainable substitute to fossil fuel [1, 2]. Consequently, a sharp increase of global biodiesel production was observed between 2004 and 2014 (fixed growth of 30 billion L). Furthermore, the European Union is the most significant biodiesel producer, which constitute of 37 % of global output [3] and according to EurObservER data, the European biodiesel consumption in EU transport sector increased from 8018 ktoe to 11603 ktoe in the last eight years [4, 5]. Moreover, this rapid growth of biodiesel production as well as consumption has been strongly policy-driven and mainly based on two factors: 1) endeavour to reduce the net climate impact of energy use, and 2) aspiration to increase the energy security in the diverse countries [6, 7]. Additionally, it is projected that the global biodiesel production should increase from 37 billion litres in 2016 to 40.5 billion L by 2026 [7].

Although biodiesel is considered as a sustainable alternative to petroleum-based fuels, however the production of biodiesel via transesterification process has by-product – crude glycerol which accounts for ~10% of the total volume of biodiesel [8-12]. In fact, crude glycerol obtained during biodiesel production contains impurities such as alcohol (typically methanol), free fatty acids (FFA), fatty acids methyl esters (FAME), organic and inorganic salts, monoglycerides, diglycerides, vegetable colours, oil, alkali metals, soaps, diols, and water [13-16]. As Yang et al. [15] indicated, the chemical composition of crude glycerol mainly varies with the type of catalyst used to produce biodiesel, the transesterification process effectiveness, recovery efficiency of the biodiesel, other impurities in the feedstock, and whether the methanol and catalysts were recovered. However, due to its impurities, crude glycerol cannot be used instead of pure glycerol in the food, pharmaceutical, cosmetics, or personal care industries [17]. Moreover, the purification of crude glycerol is economically unbeneficial. Correspondingly, various methods, including fermentation, liquefaction, digestion, steam reforming, pyrolysis, gasification are applied to convert surplus of glycerol into beneficial products, for instance alcohol, bio-oil, biogas, syngas (which mainly consists of a mixture of H_2 and CO) and hydrogen [17, 18]. Such conversion of crude

glycerol increases its market value and lead to a rise in sustainable and economic utility of biodiesel. Owing to this fact, application of plasma technologies for gasification of crude glycerol provokes great interest because conversion process is fast in time, any additional materials are not needed, and most importantly, generation of syngas are obtained. Recently Zhang et al. [19] has performed gasification of glycerol into syngas by rotating DC arc plasma and has determined that carbon conversion increased with the increase in input power, while decreased with the increase of feeding rate of crude glycerol. Moreover, energy conversion efficiency of 66% and gaseous mixture of CO (38%) and H_2 (56%) were observed. Furthermore, Yoon et al. [20] used microwave plasma to gasify crude glycerol and achieved that increasing O_2/fuel ratio causes the decrease of the cold gas efficiency as well as the syngas heating value and induces the increase of the carbon conversion. Therefore, it was observed that increasing microwave power, increases the H_2 and CO content in the syngas and it leads to increased syngas heating value, carbon conversion, and cold gas efficiency. Also, Yoon et al. [21] used a bench-scale entrained flow gasifier for utilization of the crude glycerine with air as a gasification agent. It was stated that the values of carbon conversion and cold gas efficiency increased with the excess air ratio (from 0.17 to 0.32) by more than 75% and 60%, respectively. Besides, the H_2 and CO content in the produced gases were slightly increased as the excess air ratio increased.

The purpose of this paper was to investigate air plasma suitability to decompose crude glycerol into syngas using DC thermal arc plasma torch operating at atmospheric pressure. Moreover, the impact of the diverse gasification parameters such as air flow rate and plasma torch power were investigated. Also, quantification of the gasification system in terms of the carbon conversion efficiency, cold gas efficiency, energy efficiency and specific energy requirement was estimated.

It was found that that the syngas with a lower calorific value was produced during the gasification of crude glycerol. Also, it was confirmed that the gasification effectiveness depends on the $Air/C_3H_8O_3$ ratio and the power of the plasma torch.

2. EXPERIMENTAL SETUP AND METHODOLOGY

In this research, a gasification of crude glycerol was performed using a plasma-chemical reactor. The glycerol conversion system is shown in Fig. 1 and it is comprised of an atmospheric pressure DC arc plasma torch, a power supply system, a gas supply system, a chemical reactor, a crude glycerol supply system, a condenser, and a gas chromatograph. Slightly modified experimental system was used in the previous research [22-24].
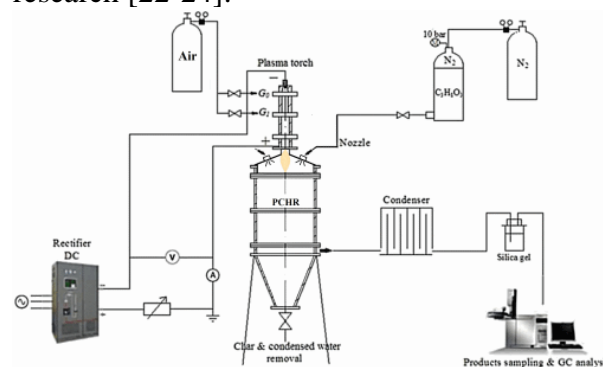

Fig. 1. Plasma-chemical crude glycerol conversion system [22]

The plasma-chemical reactor used in this research was 1 m long with the 0.4 m inner diameter. The plasma torch and the nozzles for crude glycerol supply are installed in the upper part of the reactor so that the glycerol flow is directed at an angle of 45 degrees to the plasma stream. In the middle of the reactor, an outlet chamber for the produced gaseous products is installed. At the bottom of the reactor there is a section for the removal of char and condensed water.

The atmospheric pressure DC arc plasma torch was used to generate active plasma radicals (O) from air and generate high temperature. The power of the plasma torch depends on the current intensity, voltage, and the flow rate of the plasma forming gas [23]. During the experiments, the power of the

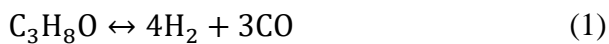plasma torch varied from 45.6 kW to 56 kW (current 160 A, voltage 285–350 V, air flow rate 2.7–4.9 g/s).

The crude glycerol (85%) containing impurities such as H_2O (9%), Na_3PO_4 (4%), CH_3OH (0.5 %) and CH_3RCOOH (1.5%) was supplied to the plasma-chemical reactor at constant rates of 2.06 g/s and 3.58 g/s, respectively, through spray nozzles. The optimal operation pressure of spray nozzle is 10 bars. Consequently, the pressure in the crude glycerol spraying line was retained by 10 bars and regulated by nitrogen gas from a cylinder. In order to increase the fluidity, spray stability and atomization of the crude glycerol, it was preheated to 343 K with a heater before the spray to the plasma-chemical reactor [24].

The produced gas was analyzed with a gas analyzer (SWG 300^{-1}), as well as gas chromatograph (Agylent 7890A) equipped with dual-channel thermal conductivity detectors (TDCs) and a valve system. Moreover, a flow meter was used after the condenser to measure the flow rate of outlet gas. Also, the flow rates of the formed products were calculated from the mass balance equation using the known flow rates of the reactants and product concentrations measured with the gas chromatograph [23].
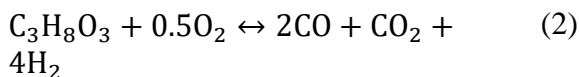
2.1. Glycerol conversion reactions

In the time of the air plasma formation, highly energetic particles such as electrons, ions and oxygen radicals were generated. These species hold the potential of degrading glycerol into useful by-product (syngas) faster. The main chemical reactions of glycerol conversion are given below [25-27]:
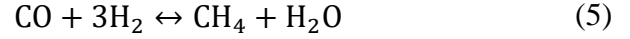
Glycerol decomposition

$$C_3H_8O \leftrightarrow 4H_2 + 3CO \qquad (1)$$

Glycerol oxidation reactions

$$C_3H_8O_3 + 0.5O_2 \leftrightarrow 2CO + CO_2 + 4H_2 \qquad (2)$$

$$C_3H_8O_3 + 1.5O_2 \leftrightarrow 3CO_2 + 4H_2 \qquad (3)$$

$$C_3H_8O_3 + 3.5O_2 \leftrightarrow 3CO_2 + 4H_2O \qquad (4)$$

Methanation

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (5)$$

2.2. Evaluation of glycerol gasification process

In order to assess the crude glycerol conversion system, it was quantified in terms of H_2/CO ratio, carbon conversion, cold gas efficiency, energy efficiency as well as specific energy requirement [28, 29]:

Carbon conversion:
$$X_C(\%) = \frac{[X_{CO}+X_{CO_2}+X_{CH_4}+X_{C_2H_2}]_{OUT}}{X_{M,IN}} \times 100\% \qquad (6)$$

Cold gas efficiency:

$$\eta_{CG} = \frac{LHV_{syngas} \times V_{syngas}}{LHV_{M,IN} \times X_{M,IN}} \qquad (7)$$

Energy conversion efficiency:

$$\eta_{eff} = \frac{(H_2+CO)_{syngas} \times LHV_{syngas}}{P_{plasma}+X_{M,IN} \times LHV_{M,IN}} \times 100\% \qquad (8)$$

Specific energy requirement:
$$SER = \frac{P_{plasma}}{(H_2 + CO)_{syngas}} \qquad (9)$$

2. RESULTS AND DISCUSSION

The effects of the air/glycerol ratio and the plasma torch power on the conversion of crude glycerol to syngas are discussed below. The concentrations of gas products for each experimental case were measured three times, giving the relative deviation below ±5%.

Crude glycerol gasification to syngas was performed at the glycerol flow rate of 5.64 g/s, air flow rate of 2.7–4.9 g/s, the plasma torch power 45.6–56 kW. The Air/$C_3H_8O_3$ ratio varied from 0.48 to 0.87.

The concentrations of gas produced after the gasification of crude glycerol are shown in Fig 2. As the Air/$C_3H_8O_3$ ratio increased from 0.48 to 0.87, the concentrations of produced gas remained practically stable. Syngas (H_2+CO) accounted for 57% (~29% of H_2 and ~27.8% of CO) out of 100% of the obtained gas. The concentrations of CO_2 and CH_4 were equal to ~6% and ~2%, respectively. The remained gases were mostly nitrogen (~33.5%) and oxygen (~1.5%).
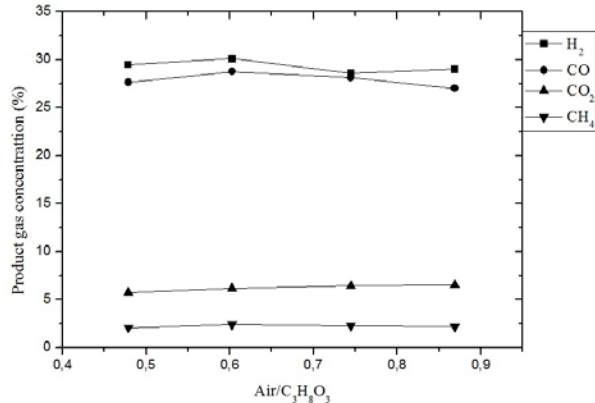

Fig. 2. Effect of the Air/$C_3H_8O_3$ ratio on the produced gas composition

Furthermore, the effect of the Air/$C_3H_8O_3$ ratio on the H_2/CO ratio was evaluated. As the Air/$C_3H_8O_3$ ratio increased from 0.47 to 0.87, the H_2/CO ratio varied from 1.02 to 1.07. Therefore, the increased Air/$C_3H_8O_3$ ratio caused negligible change in the H_2/CO ratio.

Also, the effect of the Air/$C_3H_8O_3$ ratio on the lower heating value (LHV) of the produced syngas was investigated. As the Air/$C_3H_8O_3$ ratio increased from 0.47 to 0.87, the lower heating value of the syngas slightly increased from 7.32 MJ/nm³ to 7.74 MJ/nm³. Evidently, the variation of the Air/$C_3H_8O_3$ ratio causes slightly changes of the LHV. Generally, syngas produced using air as a gasifying agent is called lower calorific value gas or "producer gas" and its heating value ranges from 4 to 7 MJ/nm³ [30, 31]. Therefore, in this experimental research the syngas with a lower calorific value of ~7.74 MJ/nm³ was produced during the gasification of crude glycerol by thermal air plasma.

Fig 3. demonstrates the effect of the Air/$C_3H_8O_3$ ratio on the carbon conversion

and cold gas efficiency. As the Air/$C_3H_8O_3$ ratio increased from 0.48 to 0.87, the carbon conversion efficiency increased from 51.3% to 75.19%, while the cold gas efficiency increased from 48.98% to 70.41%. Obtained trend shows that the increased air flow rate causes the increase in the carbon conversion efficiency as well as cold gas efficiency. Also, increased air flow rate causes the increase of the power of the plasma torch (45.6–56 kW) and this directly causes increase of the carbon conversion and cold gas efficiency. Moreover, these results are generally in the good agreement with Yoon et al. [20, 21] and Zhang et al. [19] obtained results. Yoon et al. [21] mentioned that increasing of the excess air ratio enlarges oxidation reaction as well as gasification process. Thus, carbon conversion and cold gas efficiency increases with the excess air ratio. Zhang et al. [19] established that the carbon conversion increases with the increase in input power, as well as Yoon et al. [20] determined that increasing microwave power increases the H_2 and CO content in the syngas and it causes the increase of the carbon conversion, and the cold gas efficiency.
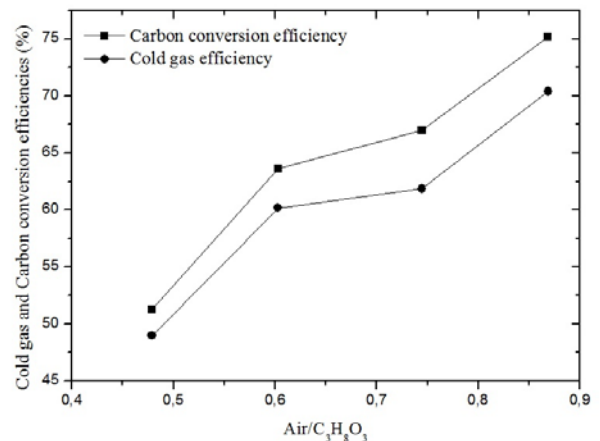

Fig. 3. Effect of the Air/$C_3H_8O_3$ ratio on the H_2 and CO gas yield and H_2/CO ratio

The effect of the Air/$C_3H_8O_3$ ratio on the crude glycerol conversion process performance in terms of energy efficiency are given in Fig. 4. As the Air/$C_3H_8O_3$ ratio increased from 0.48 to 0.87, the energy conversion efficiency increased from 29% to 41%. The optimum crude glycerol gasification to syngas process effectiveness was achieved at the η_{ef} of 41% than the flow rate of air and

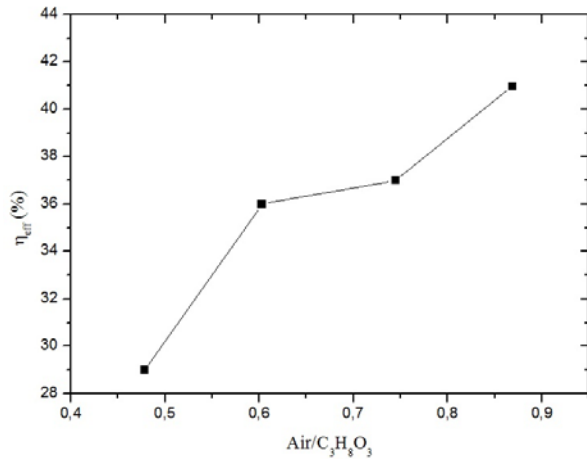the plasma torch power were at the highest value, 4.9 g/s and 56 kW, respectively.

Fig. 4. Effect of the Air/$C_3H_8O_3$ ratio on the energy efficiency

The effect of the Air/$C_3H_8O_3$ ratio on the crude glycerol conversion process performance in terms of specific energy requirements are given in Fig. 5. As the Air/$C_3H_8O_3$ ratio increased from 0.48 to 0.87, the specific energy requirements decreased from 54.16 kJ/mol to 47 kJ/mol, or from 0.502 kWh/kg to 0.435 kWh/kg. The best crude glycerol gasification to syngas process efficiency was reached at the SER of 47 kJ/mol than the flow rate of air and the plasma torch power were at 4.9 g/s and 56 kW, respectively.
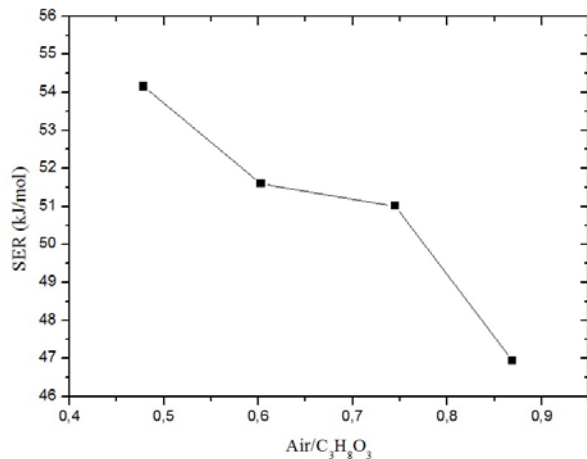

Fig. 5. Effect of the Air/$C_3H_8O_3$ ratio on the specific energy requirements

3. CONCLUSIONS

Gasification of crude glycerol into syngas using DC thermal air plasma torch was presented in this paper. The main obtained products were H_2 (~29%) and CO (~27.8%). The H_2/CO ratio changed from 1.02 to 1.07. The LHV of the produced syngas ranged from 7.32 to 7.74 MJ/nm^3 indicating that the syngas with a lower calorific value was produced during the gasification of crude glycerol. Moreover, performed study revealed that the gasification of the crude glycerol depends on the Air/$C_3H_8O_3$ ratio and the power of the plasma torch. The increased air flow rate as well as increased power of the plasma torch causes the increase in the carbon conversion efficiency and cold gas efficiency. Thus, at the maximum Air/$C_3H_8O_3$ ratio (0.87) the carbon conversion and cold gas efficiency reached 75.19% and 70.41%, respectively. Furthermore, at the highest Air/$C_3H_8O_3$ ratio, the greatest energy efficiency (41%) and specific energy requirement (47 kJ/mol or 0.435 kWh/kg) were observed.

Nomenclature
$X_{M,IN}$ Mass flow rate of injected organic material (kg/s)
X_C (%) Carbon conversion degree (%)
$X_{CO,CO_2,CH_4,C_2H_2,OUT}$ Mass flow rate of the carbon in the gas produced (kg/s)
η_{CG} Cold gas efficiency (%)
LHV_{syngas} Lower heating value of produced syngas (MJ/nm^3)
V_{syngas} Flow rate of syngas (m^3/h)
$LHV_{M,IN}$ Lower heating value of injected material (MJ/kg)
η_{eff} Energy conversion efficiency (%)
$(H_2 + CO)_{syngas}$ Mass flow rate of syngas (kg/s) In eq. (10)
$(H_2 + CO)_{syngas}$ Molar flow rate of syngas (mol) In eq. (11)
P_{plasma} Plasma torch power (W) In eq. (10)
P_{plasma} Plasma torch power (kJ) In eq. (11)

SER Specific energy requirement (kJ/mol)

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