A comparative study on syngas production from crude glycerol by utilizing DC arc plasma

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Abstract

In this study, crude glycerol conversion to syngas was investigated using thermal direct current (DC) arc plasma at atmospheric pressure. Two separate gasifying mediums were used: water vapor and air. The glycerol conversion system was quantified in terms of the H_2/CO ratio, H_2 and CO yield, carbon conversion efficiency, energy conversion efficiency, and specific energy requirements. The obtained results were compared between two studied cases as well as with other reference works. It was found that the utilization of water vapor for crude glycerol conversion to syngas showed a better overall process performance over air gasification. A 100% glycerol conversion was reached, whereas that for the air case only 75.7%. The produced syngas was of a higher calorific value (around 9.82 MJ/Nm^3) after water vapor plasma gasification. The lower heating value of syngas after air plasma gasification was around 7.32 MJ/Nm^3. The energy conversion efficiency was higher for the water vapor case exceeding 70.8% and 48.46% for the air gasification. The specific energy requirements to treat one kilogram of crude glycerol constituted 191.6 kJ/mol for the water vapor plasma and 266.45 kJ/mol for the air plasma. To sum up, it was demonstrated that syngas can be successfully produced from crude glycerol through various plasma methods (DC arc, DC rotating arc, microwave).

Keywords: syngas, crude glycerol, reforming, arc plasma, gasification, waste-to-energy.

1. Introduction

The consumption of oil has been rising due to increasing industrialization, population growth and world's economic development. As a result, a huge demand of energy, mostly derived from fossil fuels, is required to satisfy each country's needs seeking set targets for sustainable growth. However, the limited oil reserves and commitment on environmental issues through the Kyoto Protocol with further continuity steps under Paris Agreement [1] has led many researchers to explore for alternative fuels produced from renewable feedstock. Such alternative fuels could be biofuels considered as a sustainable source of fuel derived from natural biologically based materials. Ethanol generated from corn, wheat or beets and biodiesel made from oily seeds or animal fat are the most common type of biofuels [2].

Biodiesel is a liquid fuel produced predominantly from natural lipids such as vegetable oil and/or animal fat in the industrial processes called esterification or transesterification. Its properties for engine performance (better lubrication, higher cetane number and superior combustion) and environment (low in sulfur and noxious particles, better in carbon dioxide cycle in reducing greenhouse gases) render it as a more attractive fuel over diesel made from fossil fuels [3, 4]. These advantages makes biodiesel as an attractive alternative fuel to reduce global air pollution mostly generated by transportation sector.

On the other hand, biodiesel production has a side by-product – glycerol. Glycerol is a colorless, slightly sweet taste, odorless, viscous and hygroscopic liquid substance [5]. Generally, there are three pathways generating excess glycerol: hydrolysis, saponification and biodiesel transesterification [6]. However, the highest glycerol production rate is attributed to biodiesel manufacturing. Glycerol generation capacity is in close relation to biodiesel production. According to European Biodiesel Board [7] annual glycerol production in EU-28 exceeded 11.5 billion tons in 2016. The biodiesel production in 2016 was increased by 0.93% compared to 2015. Leading biodiesel producers worldwide in 2016 were: USA – 5.5 billion liters, Brazil – 3.8 billion liters, Germany, Indonesia and Argentina – 3 billion liters each, France – 1.5 billion liters, Thailand – 1.4 billion liters [8]. It is expected that global biodiesel manufacturing can reach almost 39 billion liters by 2024 [9]. Usually, glycerol accounts to 10 wt.% of the total biodiesel production, but in some cases it can amount to 30 wt.%. Therefore, despite a wide variety of industrial glycerol application in pharmaceutical, chemical, cosmetics, food and textile industries as well as explosives, tobacco etc., there will be an excess on the global market. The actions have to be taken immediately in order to avoid negative impact caused by excess glycerol utilization and storage problems.

One of the possible alternatives, it is glycerol utilization for renewable fuels production. Glycerol conversion to energy, fuels and/or chemicals have been performed in a number of research [10–16]. The main methods for glycerol reforming to hydrogen and synthesis gas production are partial oxidation (PO), steam reforming (SR), autothermal reforming (AT), and supercritical water gasification (SCWG). Some other methods such as dry reforming (DR), dry autothermal reforming and pyrolysis also were evaluated as having potential for glycerol conversion [17–20].

Despite a variety of glycerol conversion methods mentioned above, new methods are also being developed or the existing ones are being adopted. Recently, plasma gasification for glycerol conversion to hydrogen and syngas has emerged as a promising utilization method. Utilization of plasma for waste-to-energy treatment may overcome shortcomings of the traditional conversion methods. In a particular case, plasma offers advantages over traditional glycerol conversion methods due to avoidance of catalysts, use of rare earth metals for their preparation, catalyst sensitivity to contamination and deactivation, high pressures, feedstock pretreatment etc. [21].

Since plasma is a fourth state of matter, it can be distinguished into two main groups depending on the temperature: high temperature (above 5×10^4 K) and low temperature plasmas (below 5×10^4 K). The high temperature, or fusion, plasma is a plasma which naturally exist in space, sun, etc. Therefore, the low temperature plasma can be subdivided into the thermal plasmas characterized by a local thermodynamic equilibrium (LTE) between charged particles (electrons and ions), and the non-thermal (or cold) plasmas which is in a non-equilibrium state (non-LTE) [22]. Direct current (DC), radio frequency (RF) and microwave (MW) plasma are a few examples of typically used thermal plasma for waste treatment. Due to very high temperatures (10^3–10^4 K), a wide range of operating power levels (from 1 kW to 50 MW), easy process control *in-situ*, relatively smaller installation size, possibility to heat oxidative, reductive, inert gases and their mixtures directly, and etc., thermal plasma technology can realize many cleaner processes in waste treatment, material synthesis and processing, and other processes.

There are very few studies on glycerol conversion to syngas by utilizing plasma. Yoon et al. [23] investigated hydrogen and synthesis gas production from glycerol by utilizing a 2 kW microwave plasma system. Various effects such as O_2/fuel ratio, H_2O/fuel ratio and MW power on glycerol conversion efficiency were investigated. The highest H_2 and CO content, 57% and 35%, respectively, was obtained at the zero O_2/fuel ratio, constant H_2O/fuel ratio at 0.8 and MW power of 1.6 kW. At these conditions, the lower heating value of the produced syngas, the cold gas efficiency and the carbon conversion efficiency were around 12 MJ/Nm^3, ~99% and ~80%, respectively. Zhang et al. [24] performed experimental research on crude glycerol conversion into syngas by a 24.1 kW rotating DC arc plasma. The effects on plasma power, glycerol feeding rate and water content in feedstock were investigated. It was found that the producer gas contained mainly of H_2 and CO with concentrations 56% and 38%, respectively. Additionally, small amounts of CH_4, C_2H_4 and C4 hydrocarbons were also obtained. Complete carbon conversion with the highest energy conversion efficiency of 66% were determined under the input plasma power of 17.1 kW, 30 g/min glycerol feeding rate, 2 Nm^3/h argon flow rate and 0.077 T magnetic flux intensity. Authors concluded that a rotating DC arc plasma is a promising method for syngas production from crude glycerol.

In this paper, a crude glycerol conversion to syngas using DC arc plasma was experimentally investigated. The experiments were performed under two different plasma forming gases: water vapor and air. This effect was the only one parameter enabling to directly compare the obtained results between. In order to evaluate the performance of the crude glycerol conversion in water vapor and air plasmas, separately, the systems were quantified in terms of the producer gas composition, H_2 and CO yield, H_2/CO ratio, the lower heating value, carbon conversion, energy efficiency and specific energy requirements. Glycerol conversion to syngas in water vapor plasma showed a better overall process performance over the air plasma used.

2. Materials and methods

2.1. Feedstock

A crude glycerol with purity of 85% and water content of 9% was used as a feedstock for synthesis gas production. It was received from the JSC “Rapsoila” specializing in biodiesel production from rapes. Due to the specifics of the transesterification process producing biodiesel, the remaining crude glycerol contains impurities such as CH_3OH, Na_3PO_4 and CH_3RCOOH with concentrations 0.5%, 4% and 1.5%, respectively. Therefore, the chemical formula of crude glycerol looks like as follows:

$$\overset{85wt\%}{C_3H_8O_3} + \overset{9wt\%}{H_2O} + \overset{0.5wt\%}{CH_3OH} + \overset{4wt\%}{Na_3PO_4} + \overset{1.5wt\%}{CH_3RCOOH}\,. \qquad (1)$$

Since Na_3PO_4 is being used as a heterogeneous catalyst in the transesterification process of fatty oil, some white agglomerated spots of salt were detected on the walls of the reactor and the pipes of the producer gas cooling system. The proximate and ultimate analysis of crude glycerol is shown in Table 1.

Table 1. Proximate and ultimate analysis of crude glycerol

Proximate	
Carbon, %	20.15±0.19
Hydrogen, %	5.64±0.29
Nitrogen, %	< 0.01
Sulfur, %	< 0.01 (0.002)
Oxygen*, %	65.87
Chlorine, %	0.02±0.001
Ultimate	
Volatile matter, %	78.98±1.0
Fixed carbon, %	< 0.01

Ash, %	8.34±0.02
Moisture, %	12.49
Lower heating value	14.36±0.03

*by difference

The feedstock was supplied through the special spray nozzles at a constant flow rate of 5.6 g/s. The operational pressure in the glycerol feeding line is 10 bars. Before the supply into the plasma-chemical reactor, it was slightly preheated to about 70 ^{o}C to reduce viscosity and improve the spray stability and atomization.

2.2. Experimental setup

The experimental setup used in this study is shown in Figure 1. The main parts of the system are as follows: plasma torch (1), chemical reactor (2), plasma-forming gas feeding line (3), electrical circuit (4), glycerol feeding line (5), and product gas analysis (6). A more detailed presentation of the experimental setup is described in previous works [25, 26].

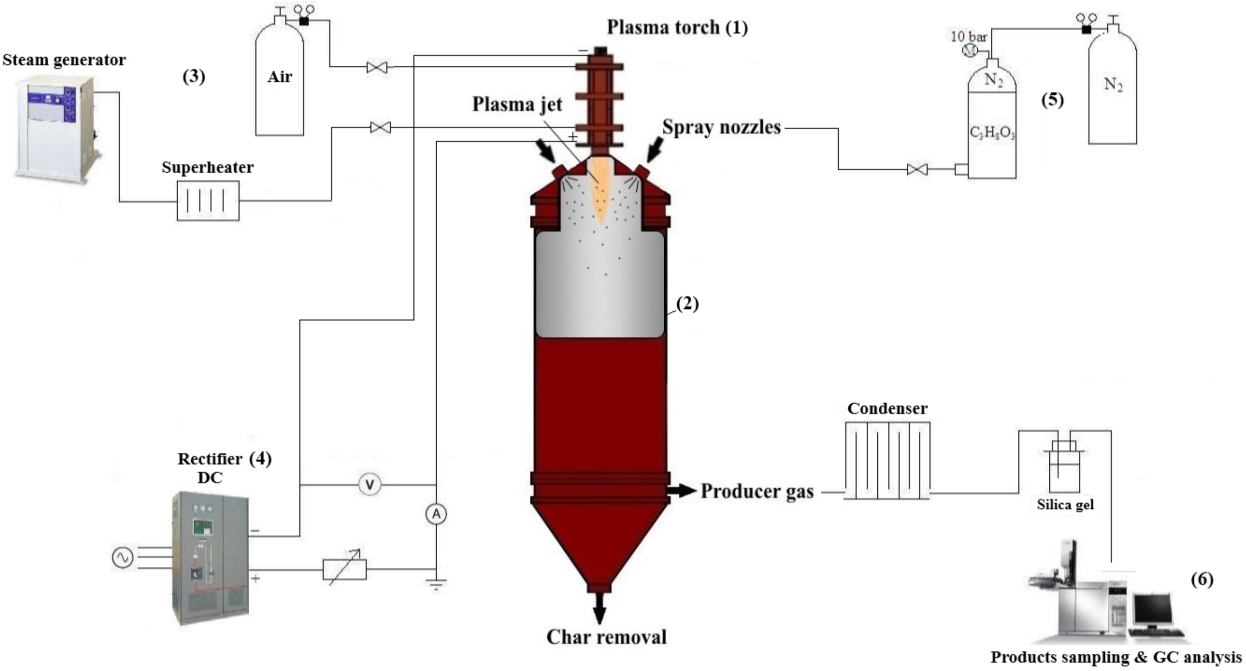

Fig. 1 Experimental setup of glycerol conversion system

Nonetheless, the main difference of this research work is that the experiments were performed using different plasma-forming gases (water vapor and air) at the other parameters such as the arc current intensity and the glycerol flow rate being equal at 160 A and 5.6 g/s, respectively. The geometry of the plasma torch was also the same in both cases.

The formed gaseous products were analyzed by means of an Agylent 7890A gas chromatograph (GC) equipped with a dual-channel thermal conductivity detectors and a valve system. A gas analyzer SWG 300^{-1} was also utilized to measure the concentrations of formed gaseous products *in-situ* and compare with the GC. The relative error of the obtained results were within the limits and was below ±5%. Each experimental point was measured at least three times.

2.3. Main chemical reactions

The main crude glycerol conversion reactions are summarized and shown in Table 2. However, before the 'traditional' glycerol conversion reactions, firstly, the initiation of these reactions might be caused or supported by the energetic particles (electrons, ions, radicals, etc.) created by high temperature electric arc of the plasma torch and/or thermochemical effect. The thermochemical effect may appear due to the heating of the surrounding gas (water vapor or air) present around the electric arc [27, 28]. On the contrary, some researchers believe that the induced active species in thermal plasma doesn't play any significant role on increasing the chemical kinetics and reaction rate. As a consequence, acceleration of chemical reactions is mostly based on the thermal effect of the high temperature plasma stream due to the local thermodynamic equilibrium between the electrons and ions. The mean free path of electrons or other species is too short to initiate such reactions. It is believed that the non-thermal plasma may be an option as it is more selective for high energy electrons (up to tens of eV) generation. However, such plasma is mostly suitable for gas cleaning, but not for waste treatment applications. Another option could be the use of discharges such as a gliding arc characterized by both LTE and non-LTE conditions. Generally, thermal plasma is mostly suitable for liquid and solid organic waste treatment.

Table 2. Main glycerol conversion reactions [11, 21]

Steam reforming (SR):	$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$	+ 122.83 kJ/mol	(R1)
Partial oxidation (PO):	$C_3H_8O_3 + 0.5O_2 \rightarrow 2CO + CO_2 + 4H_2$	– 31.8 kJ/mol	(R2)
	$C_3H_8O_3 + 1.5O_2 \rightarrow 3CO_2 + 4H_2$	– 597.7 kJ/mol	(R3)
Complete oxidation (CO):	$C_3H_8O_3 + 3.5O_2 \rightarrow 3CO_2 + 4H_2O$	– 1565 kJ/mol	(R4)
Water–gas shift (WGS):	$CO + H_2O \leftrightarrow CO_2 + H_2$	– 41.2 kJ/mol	(R5)
Cracking (pyrolysis):	$C_3H_8O_3 \rightarrow 3CO + 4H_2$	+ 251 kJ/mol	(R6)
Methanation/hydrogenation:	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	– 206 kJ/mol	(R7)
Methanation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	– 165 kJ/mol	(R8)
Hydrogenolysis:	$2C_3H_8O_3 + H_2 \rightarrow 3CH_4 + 3CO_2 + 3H_2O$		(R9)

Despite the main reactions, the glycerol conversion to syngas might be affected by side reactions as well. The later influence will be neglected and not discussed within the paper as less important reactions.

2.3. Conversion process performance evaluation

In order to evaluate the process performance and compare with other methods, generally some common measures are being used, such as the H_2 and CO yield, the H_2/CO ratio, the lower heating value of produced syngas, the carbon conversion efficiency, the energy conversion efficiency, and the specific energy requirements [23, 24, 29]. Each value is defined below.

The H_2 and CO yield:

$$H_2(yield) = \frac{m_{H_2,OUT}}{m_{fuel}} \times 100\%, \tag{2}$$

$$CO(yield) = \frac{m_{CO,OUT}}{m_{fuel}} \times 100\%, \tag{3}$$

where $m_{H_2,OUT}$ and $m_{CO,OUT}$ is the mass flow rates of hydrogen and carbon monoxide produced (kg/s), respectively. m_{fuel} is the mass flow rate of the reaction products (kg/s).

The H_2/CO ratio shows the quality of syngas. It’s an important ratio showing the ability and availability to produce value-added products from syngas such as chemicals (methanol, biomethane, and hydrogen), biodiesel via Fisher–Tropsch (FT) pathway and/or energy (thermal, electrical). The higher the ratio, the better the quality of syngas is.

The lower heating value (LHV):

$$LHV(syngas) = 10.78H_2(\%) + 12.63CO(\%) + 35.88CH_4(\%) + ... + XC_xH_y(\%), [MJ/Nm^3], \tag{4}$$

where $H_2(\%)$, $CO(\%)$, $CH_4(\%)$, $C_xH_y(\%)$ are the content of gaseous products in producer gas.

The carbon conversion efficiency (CCE):

$$CCE(\%) = 12 \times Y_{dry\ gas} \times \left\{ \frac{[CO + CO_2 + CH_4] + 2 \times [C_2H_2 + C_2H_4 + C_2H_6]}{22.4 \times C} \right\} \times 100\%, \tag{5}$$

where $Y_{dry\ gas}$ is a dry gas yield in Nm^3 per kg of dry feedstock (Nm^3/kg), CO, CO_2, CH_4, C_2H_2, C_2H_4 and C_2H_6 are in % (v/v), and C is in % of carbon in dry feedstock.

The energy conversion efficiency (ECE):

$$ECE = \frac{m_{syngas} \times LHV_{syngas}}{P_{plasma} \times \eta + m_{fuel} \times LHV_{fuel}} \times 100\%, \tag{6}$$

where m_{syngas} and m_{fuel} are the mass flow rates of product gas and feedstock (kg/s), respectively. LHV_{syngas} and LHV_{fuel} are net calorific values of product gas and feedstock (MJ/kg), respectively. *P* is a plasma torch power (kW), and η is the thermal efficiency of plasma torch.

The specific energy requirements (SER):

$$SER = \frac{P}{m_{syngas}}, \tag{7}$$

where SER is the specific energy requirement (kJ/mol or kWh/kg), *P* is the plasma torch power (kJ/s), m_{syngas} is the mass flow rate of syngas gas (mol/s).

3. Results and Discussion

3.1. Crude glycerol conversion in water vapor and air plasmas

Due to water vapor and air used as the plasma-forming gases and gasifying agents, the ratio of the gasifying agent-to-glycerol (gasifying agent/$C_3H_8O_3$ ratio) was the only one common parameter for both cases enabling to compare the obtained experimental results between. The summarized experimental conditions for both cases are shown in Table 3.

Table 3. Experimental conditions for crude glycerol conversion

Parameter/Case	**Water vapor + glycerol**	**Air + glycerol**
Arc current, A	160	160
Arc voltage, V	350–390	350
Power, kW	56–62.4	45.6–56
Glycerol flow rate, g/s	5.6	5.6
Gasifying agent flow rate, g/s	2.9–5.15	2.7–4.9
T_{plasma}, K	2800	4400
Plasma torch thermal efficiency (η)	0.69–0.76	0.6–0.74

As could be seen from the above table, a change in the flow rate of the gasifying medium was the only one parameter affecting the crude glycerol conversion process. The variation of the flow rate of the gasifying medium directly affected the voltage drop and the power of the plasma torch at the constant electric arc current intensity of 160 A. This is because of the physical properties (enthalpy, thermal and electrical conductivity, etc.) of water vapor and air. Therefore, the mean temperature of the plasma stream entering the chemical reactor differed significantly. However, the higher temperature of air plasma was not the crucial parameter over water vapor gasification. In this section it will be shown, that the use of water vapor gave a better overall process performance.

In both cases, the producer gas was mainly consisted of H_2 and CO as well as small amounts of CO_2 and CH_4 (Fig. 2). However, a relatively high amount of N_2 (33 vol.%) was observed in the case of air used. Since nitrogen comprises the highest share in the composition of air, it's impossible to avoid ballast nitrogen and its compounds (NO_x) in the producer gas. The concentrations of NO_x was below 1%. This is a reason why the use of air as a gasifying medium is not the best choice due to nitrogen dilution in the producer gas. As could be seen in Fig. 2, N_2 (up to 5.5 vol.%) was also observed in the case of crude glycerol conversion to syngas in the ambient of water vapor. This was because a small amount of air (up to 10–17%) was used near the hafnium cathode of the plasma torch in order to avoid its erosion. Generally, the combination of water vapor with glycerol yielded a higher concentration of H_2+CO produced, accounting to around 76 vol.% over 56 vol.% in the case of air used. Steam reforming (R1) and pyrolysis (R6) reactions are more favorable at higher temperatures (over 1000 K) and enables to produce higher concentrations of H_2 and CO instead of partial oxidation (R2, R3) and complete oxidation (R4) reactions, which plays a key role below 1000 K. Lin [30] indicates that glycerol pyrolysis and steam reforming reactions become more and more thermodynamically favorable as temperature increases. However, the concentration of CO_2 was lower in the case of air used, indicating that the PO was in favor over CO reaction. The equivalence ratio (ER) was in the range of 0.09–0.17, indicating an oxygen starved environment. Whereas, in the case of water vapor used, a higher concentration of CO_2 (13.45 vol.%) was observed to due water–gas shift (R5) and hydrogenolysis (R9) reactions.

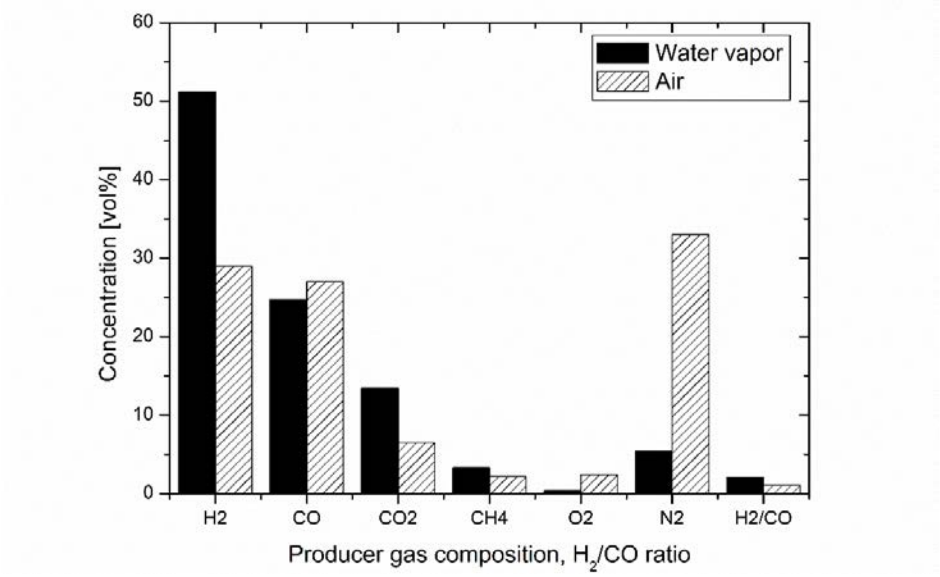

Fig 2 Elemental composition of the producer gas and the H_2/CO ratio

The H_2/CO ratio was higher in the case of water vapor used as a gasifying agent and exceeding 2.07. The ratio indicates that the produced syngas is suitable for direct biodiesel production via Fisher–Tropsch synthesis and no adjustment is required. A desired H_2/CO ratio for biodiesel production is 2:1 [30]. The H_2/CO ratio was almost stable around 1.07 in the case of air plasma gasification of crude glycerol. It doesn't changed significantly as the air flow rate and the power of the plasma torch changed. A lower H_2/CO ratio was determined by a lower H_2 concentration in the producer gas because of the dominance of oxidation reactions (R2–R4) theoretically yielding maximum 4 moles of H_2 instead of 7 moles in SR (R1).

Figure 3 shows the yield of hydrogen and carbon monoxide formed after the crude glycerol gasification. It could be seen that as the gasifying agent-to-glycerol ratio increased from 0.48 to 0.92, the yield of H_2 and CO increased for both cases. The curve trends of yields were almost the same for crude glycerol gasification in water vapor and air. Thus, the H_2 yield increased from 27.8% and 30% to 42% and 43, respectively. Whereas, the CO yield increased from 32.56% and 37.54% to 55.7% and 53.4%, respectively. The endothermic glycerol pyrolysis reaction (R4) and exothermic glycerol PO reaction (R2) are the only two heterogeneous reactions where CO can directly come from. The rest is formed during homogeneous exothermic WGSR (R5) and methanation reaction (R7).

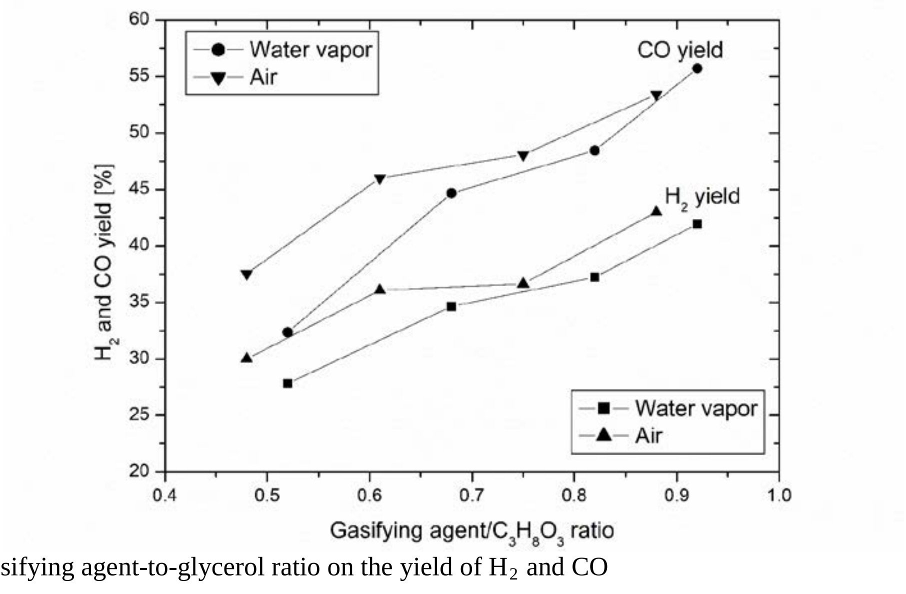

Fig 3 Effect of gasifying agent-to-glycerol ratio on the yield of H_2 and CO

The LHV in both cases was not changing significantly due to the stable concentrations of gaseous compounds in the producer gas. The LHV of syngas produced after crude glycerol conversion in the ambient of water vapor plasma was around 9.82 MJ/Nm^3, whereas that in the air plasma case 7.32 MJ/Nm^3. A lower LHV of syngas produced in the air was mostly affected by the presence of ballast nitrogen and its dilution in the producer gas.

Figure 4 illustrates the effect of gasifying agent-to-glycerol ratio on the carbon conversion efficiency. It showed that increasing gasifying agent-to-glycerol ratio would lead to a higher carbon conversion for both cases. However, a full carbon conversion was reached only in the case of water vapor gasification of crude glycerol. The highest value for the air plasma gasification amounted to 75.7%. The increasing flow rate of plasma-forming gas (water vapor or air) at a constant arc current intensity would lead to a rise in an electric arc's voltage drop, and therefore, the power of the plasma torch increases. Therefore, the higher input power of the plasma torch could lead to a higher energy density as well as temperature, which is beneficial for glycerol valorization.

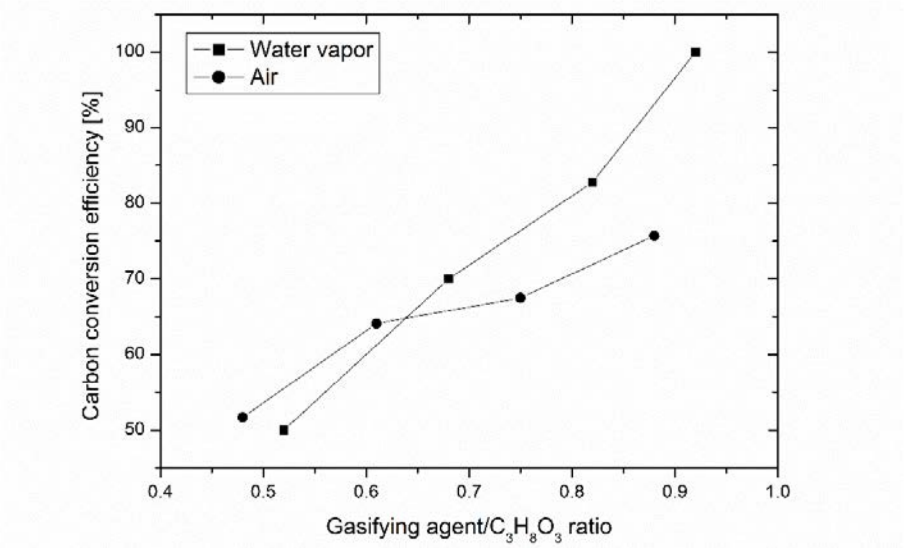

Fig 4 Effect of gasifying agent-to-glycerol ratio on the carbon conversion

Another important parameter showing the conversion process performance and efficiency is the energy conversion efficiency, which defines the ratio between the chemical energy of the produced syngas and chemical energy of the feedstock including external plasma energy input. Therefore, the effect of gasifying agent-to-glycerol ratio on the energy efficiency is shown in Fig. 5.

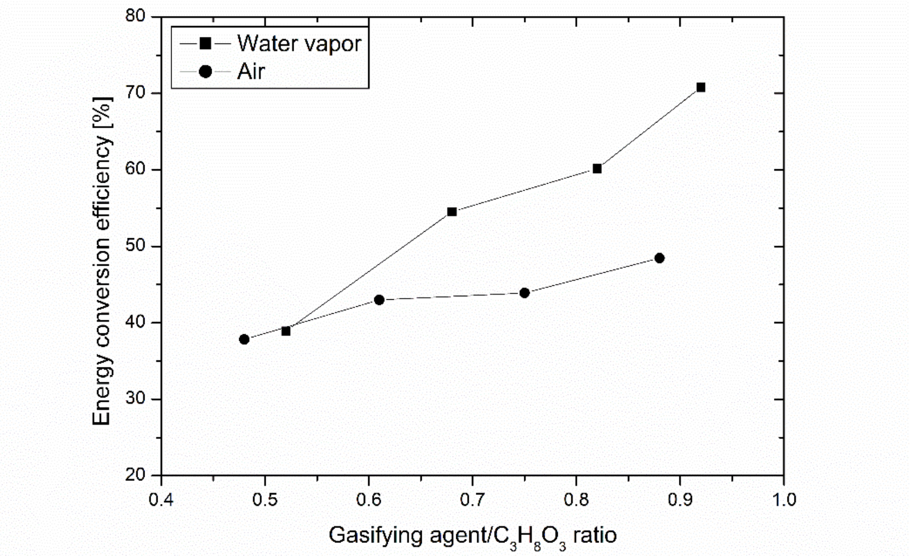

Fig 5 Effect of gasifying agent-to-glycerol ratio on the energy conversion efficiency

The obtained experimental data showed that the water vapor plasma gasification of crude glycerol was more efficient than the air plasma gasification. This was mainly attributed to the gasifying medium used, which yielded the higher amount and better quality of syngas produced in terms of quantity and lower heating value. Since the power of the plasma torch is a limiting factor for a higher ECE, nonetheless, the increased power due to the increase in the flow rate of the gasifying medium induced the ECE to rise in both cases studied. However, the increase of the ECE in the case of air plasma was much lower and the curve is smoother compared to the water vapor used as a plasma-forming gas and gasifying agent, simultaneously. The highest ECE for both cases were obtained at the gasifying agent-to-glycerol ratio of 0.9 exceeding 70.8% for the water vapor case and 48.46% for the air gasification.

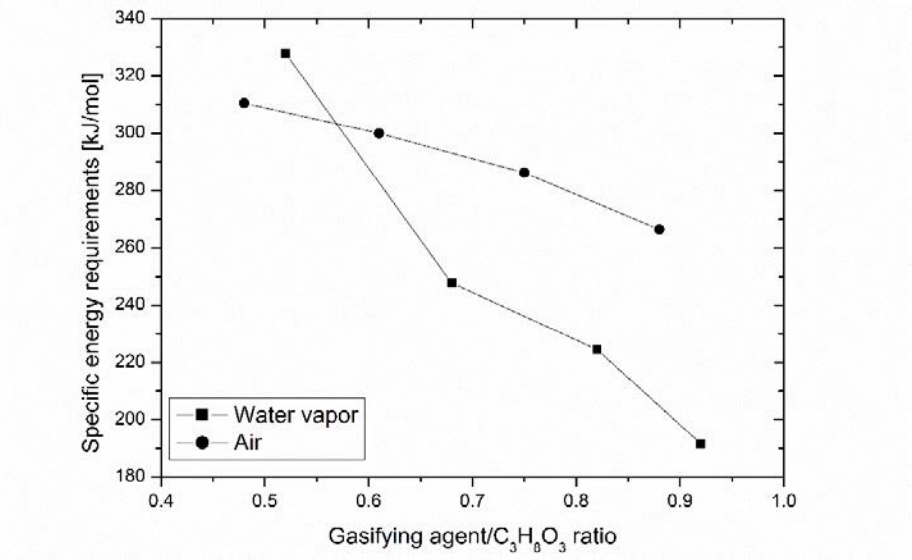

Fig 6 Effect of gasifying agent-to-glycerol ratio on the specific energy requirements

The effect of the gasifying agent-to-glycerol ratio on the specific energy requirements was also studied and is shown in Fig. 6. In spite of that the power of the plasma torch was higher using water vapor as the plasma gas and gasifying medium, the energy required to treat one kilogram of crude glycerol to syngas was lower (Eq. 7). The curve decreased more sharply as compared to the air gasification case. Only at the gasifying agent-to-glycerol ratio of 0.5, the SER was higher around 17.37 kJ/mol for the water vapor case. The lowest SER was achieved at the gasifying agent-to-glycerol ratio of 0.9. For the water vapor used it was 191.6 kJ/mol (or 1.78 kWh/kg), whereas that for the air amounted to 266.45 kJ/mol (or 2.5 kWh/kg). This was mainly affected due to a higher amount of syngas produced, i.e. more H_2 and CO were produced via SR (R1), pyrolysis (R6) and WGSR (R5) reactions using water vapor plasma.

3.2. Comparison between results

This section summarizes the experimental results obtained in this study and also compares with other research works performed by Yoon et al. [23] and Zhang et al. [24] on the same topic with the same method (Table 4).

Table 4. Summary of the crude glycerol conversion to syngas with various plasma methods

Parameter/Reference	**This study (water vapor + glycerol)**	**This study (air + glycerol)**	**Yoon et al. [23]**	**Zhang et al. [24]**
Discharge type	DC arc	DC arc	MW	Rotating DC arc
Power, kW	62.4	56	2	24.1
Thermal efficiency (η), (%)	76.1	74.1	n.d.	40
Gasifying agent	Water vapor (83%)/Air (17%)	Air	Air/steam	Ar/water in glycerol
H_2, (vol.%)	51.16	29.00	57	56
CO, (vol.%)	24.74	27.00	35	38
H_2/CO ratio	2.07	1.07	1.63	1.47
LHV_{syngas}, MJ/Nm^3	9.82	7.32	12	11
CCE, (%)	100	75.7	~100	100
ECE, (%)	70.8	48.46	62*	66
SER, (kJ/mol)	191.6	266.45	n.d.	n.d.

*This value was named as the cold gas efficiency. The power of the plasma was not added to the formula presented. If the power were added, the ECE would be lower.

Regarding the obtained results in this research gasifying crude glycerol and after comparing them between, it was revealed that the use of water vapor as a gasifying agent and plasma-forming gas gave a better overall process performance almost in all the parameters studied. This is because steam reforming (R1) reaction enables to provide a higher quantity of hydrogen in the producer gas instead of partial oxidation (R2, R3) does. Moreover, SR is more favorable above 1000 K. Since the mean plasma temperature in the reaction zone with the sprayed crude glycerol was always higher than 1000 K, this feature render a better performance of the system. The phenomenon of plasma also induced reaction kinetics and selectivity for a higher amount of syngas production. The use of air as a plasma-forming gas and gasifying agent yielded a higher amount of ballast nitrogen and NO_x compounds in the producer gas. Therefore, this affected the process efficiency giving a lower process parameters.

Since the power of the plasma torch was highest in this study, however, the use of a microwave plasma [23] and a rotating arc discharge [24] allowed to generate higher concentrations of syngas. This is also depended on the process conditions in each study. However, the H_2/CO ratio (2.07), suitable for biodiesel or chemicals production, was observed to be higher in this experimental research. This ratio could be adjusted by WGSR reaction (R5). After glycerol conversion, the lower heating value of syngas was higher for both cases compared. This was mostly influenced by a much higher CO and H_2 concentrations in the producer gas observed after glycerol treatment in the MW and the rotating DC arc discharge plasmas. In all studied cases, a full carbon conversion was reached, indicating that glycerol was fully converted to syngas and other by-products. Furthermore, the energy conversion efficiency was almost the same in all the cases, expect the air plasma gasification. Nonetheless, the summarized results show that there is a great potential of plasmas (arc discharge, rotating arc discharge, MW) to be applied for glycerol conversion to syngas. Further studies are required optimizing glycerol conversion process, thus getting as much syngas as possible.

Conclusions

In this study, crude glycerol conversion to syngas was investigated using thermal DC arc plasma at atmospheric pressure. Two separate gasifying mediums were used: water vapor and air. The performance of the glycerol conversion system was quantified in terms of the H_2/CO ratio, H_2 and CO yield, carbon conversion efficiency, energy conversion efficiency, and specific energy requirements. The obtained experimental results were compared between as well as with other reference works. It was found that a full crude glycerol conversion to syngas was reached using water vapor as a gasifying medium and plasma-forming gas. Generally, crude glycerol gasification in water vapor gave a better process performance and syngas quality over the air plasma gasification. After the comparison with other reference works it was determined that H_2 and CO concentrations in the producer gas were lower in this study, thus yielding a lower heating value of syngas. However, the energy conversion efficiency was slightly higher in the studied case, except for air plasma gasification. The use of plasma for glycerol conversion to syngas is a promising method, which requires further investigation on process optimization.

Acknowledgements

Travel expenses to the conference is funded by the European Social Fund under the No. 09.3.3-LMT-K-712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure (grant No. DOTSUT-78, 09.3.3-LMT-K712-06-0162). The research was funded by the European Regional Development Fund according to the supported activity “Research Projects Implemented by World-class Researcher Groups” under Measure No. 01.2.2-LMT-K-718 (grant No. 01.2.2-LMT-K-718-01-0005) from the Research Council of Lithuania.

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