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Effect of catalyst on the producer gas composition from co-gasification of glycerol/fat mixtures

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Abstract

In this work, steam reforming of crude glycerol and animal fat mixtures was studied. The tests were carried out at temperatures of 700 °C and 750 °C in a fixed bed reactor using activated alumina or dolomite particles, to evaluate the catalytic capacity of these minerals in the removal of tar from the producer gas. The gas produced was quantified and analyzed by gas chromatography, and it was concluded that its composition is greatly influenced by the bed material used. The results obtained showed that dolomite is more effective in reducing the tar content, evidencing its ability to catalyze the tar reform reactions and promoting the water-gas shift reaction. Consequently, using dolomite as a catalyst, a producer gas with 47–48 vol% in H_2 and 27–30 vol% in CO_2 was obtained, while using a bed of alumina particles, a gas with a high CO content (45–48 vol%) and lower H_2 content (34–37 vol%) was produced.

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Keywords: Alumina; Dolomite; Fat; Co-gasification; Glycerol; Steam reforming

1. Introduction

In the global energy and environmental landscape, there has been an increase in the dynamics inherent in the move to renewable energy sources. The possibility of valuing waste is presented as a fundamental strategy in the context of environmental and economic sustainability, contributing to the model of transition to a circular economy and intensifying the use of renewable energy sources.

In Portugal, there are by-products and industrial wastes for which it is urgent to find alternatives that aim at their recovery. In this context, the present study intends to evaluate the technical feasibility of the gasification process of two industrial by-products/wastes: crude glycerol from the biodiesel industry and animal fat from the leather industry. In this work the results of the effect of the use of dolomite as a catalyst in the composition of the produced gas are presented.

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Despite the advances achieved in recent years in the design of more efficient gasifiers, the cleaning process of the gas produced is still a limitation on the use of biomass for electricity generation. The presence of tars (condensable organic compounds) in the producer gas can cause clogging and corrosion and reduce the overall efficiency of the process. For this reason, interest in the catalysis of biomass gasification has grown in recent decades. Dolomite is a biomass gasification catalyst that has been studied by several researchers [1–4]).

Delgado et al. [5] investigated the use of Norte dolomite for the steam reforming of biomass tars. They reported that the tar conversion increased with increasing temperature and complete elimination was observed at 840 °C. They observed that an increase in the gas/catalyst contact time and in particle size results in an increase in the destruction of the tar present in the gas and in more H_2 and CO_2 produced.

Peréz et al. [6] investigated the biomass gasification in a bubbling fluidized bed gasifier using steam–oxygen mixtures as gasification agent and calcined dolomite located downstream from the gasifier. They have reported an increase in the H_2 content, a decrease in the CO content and a tar conversion of 90–95 vol% with space times of 0.06–0.15 kg calcined dolomite/(hm^3).

Gil et al. [7] investigated the performance improvement of a fluidized-bed biomass gasifier, by in-bed use of calcined dolomite. They reported that 15–30 wt% of (calcined) dolomite in the bed improves quite a lot the quality of the producer gas, presenting a tar content below 1 g/m^3 and an increase in the H_2, CO and CH_4 contents.

Andrés et al. [8] studied the catalytic gasification of sewage sludge in a fluidized bed reactor using air and air–steam mixtures as the gasification agent. The aim of the study was to study the influence of three catalysts: dolomite, olivine and alumina in the composition of the producer gas and in the production of tars during the gasification process. The results showed that dolomite has the greatest activity in the elimination of tar, followed by alumina and olivine, and it was found that the concentration of tar decreased by 75% using dolomite against 65% using alumina. The study also indicates that at 800 °C dolomite allows to obtain a higher amount of hydrogen (17%) when compared to alumina (1 5%) and that the highest H_2/CO ratio was obtained using dolomite.

Pinto et al. [9] studied the gasification of lignin-rich solids in a bubbling fluidized bed gasification reactor where 33% by mass of minerals such as limestone, dolomite or olivine were added to the silica sand bed. In the study, the effect of the presence of these minerals on the synthesis gas composition was analyzed. They concluded that the highest concentrations of H_2 and CO_2 and the lowest CO levels were obtained in the presence of dolomite. They also concluded that dolomite seems to be the most suitable catalyst to promote the destruction of tars.

Gasification is a thermochemical process involving an oxidant agent and consisting of a partial oxidation that allows the conversion of carbonaceous raw material into a gaseous fuel. The reaction mechanism of the gasification process is complex, and reactions 1 to 10 are some of the main reactions involved in the process [10–12]:

Water–gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_r^{298\ K} = -41.2\ kJ/mol \tag{1}$$

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H_r^{298\ K} = +172.58\ kJ/mol \tag{2}$$

Steam char reaction:

$$C + H_2O \rightleftharpoons CO + H_2 \quad \Delta H_r^{298\ K} = +131\ kJ/mol \tag{3}$$

Methane steam reforming:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H_r^{298\ K} = +206\ kJ/mol \tag{4}$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad \Delta H_r^{298\ K} = +165\ kJ/mol \tag{5}$$

Methane dry reforming:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H_r^{298\ K} = +247\ kJ/mol \tag{6}$$

Tar reactions: $\Delta H_r^{298\ K} = +[200 - 300]\ kJ/mol$

Thermal cracking:

$$pC_nH_x \rightarrow qC_mH_y + rH_2 \tag{7}$$

Tar steam reforming:

$$C_nH_x + nH_2O \rightarrow \left(n + \frac{x}{2}\right) H_2 + nCO \quad (8)$$

Tar dry reforming:

$$C_nH_x + nCO_2 \rightarrow \frac{X}{2} H_2 + 2nCO \quad (9)$$

Tar carbon formation:

$$C_nH_x \rightarrow \frac{X}{2} H_2 + nC \quad (10)$$

2. Materials and methods

The co-gasification of crude glycerol/fat mixtures was studied in a down flow fixed bed reactor using steam as the gasification agent. Tests were performed with a fixed bed composed of catalyst particles of dolomite (2 to 5 mm of diameter) or alumina (6 mm of diameter). The results obtained with dolomite were compared with the ones obtained using alumina particles. The experimental tests were performed at 700 °C and 750 °C using a mixture composed by 59% of glycerol, 3% of fat and 38% of water, having a C/H2O mass ratio of 0.72. Details on the experimental installation and test procedure can be found in Almeida et al. [13].

Dolomite ($MgCO_3CaCO_3$) is one of the most common materials used as a catalyst in biomass gasification [14]. Dolomite is used with the main objective of reducing the tar content in the producer gas and its main operating problem is its fragility when calcined. The calcination of dolomite above 750 °C gives rise to the formation of MgO (21.3%) and CaO (30.4%) due to the loss of CO_2.

After the gasification tests, the bed of alumina particles was calcinated at 900 °C during 30 min and the dolomite bed was calcinated at 550 °C during 2 h, to remove the deposited carbonaceous residue. The lower calcination temperature, in the case of dolomite, was selected to prevent the CO_2 mass loss with the consequent material fragilization.

3. Results and discussion

In Fig. 1 the results obtained for the average gas and liquid phase yields are presented for the two particle bed materials studied. These indicators represent the fraction of the feed that was converted to the gaseous phase and the one that remained in the condensed phase. The gaseous phase, called producer gas, is essentially composed of H_2, CO, CH_4 and CO_2 and the liquid phase consisting of the condensable fraction of the gas produced in the gasification process, is composed mainly by water and tars (aromatic hydrocarbons).

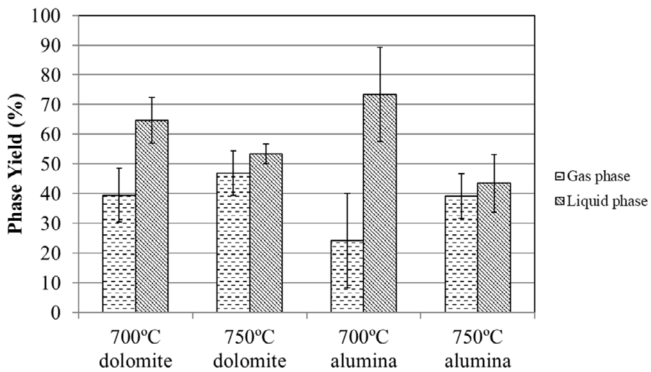

Fig. 1. Gas and liquid phase yields.

The results obtained clearly show that when is used a bed of dolomite particles the gas phase yield is greater than that obtained when using alumina particles. They also show that the increase in temperature favors the production of the gas phase and the decrease of liquid phase production, for both materials studied. The determination of phase yields is affected by a large experimental error (standard deviation indicated as vertical bars in Fig. 1) however they are indicators of the behavior of the co-gasification process under the studied conditions.

The effect of temperature and bed material on the producer gas composition was studied. Fig. 2 shows the obtained results for CO, CO_2, H_2 and CH_4.

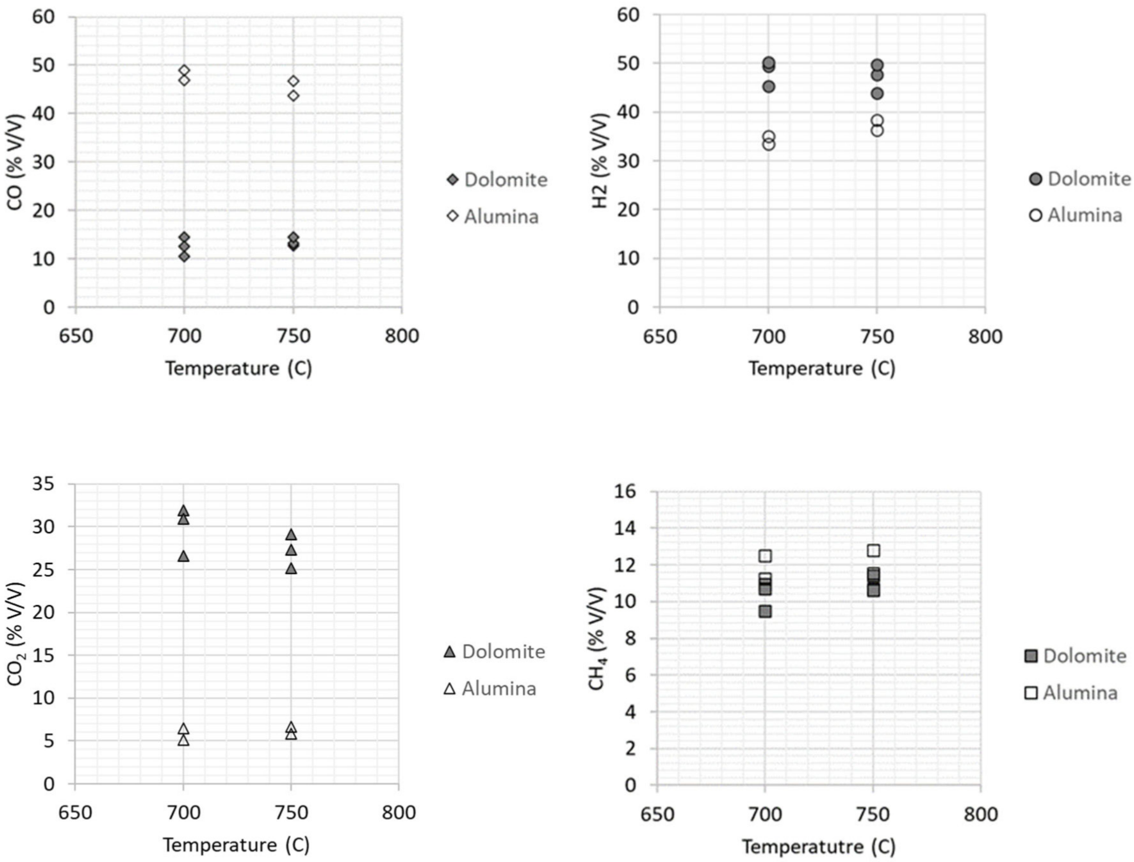

Fig. 2. Producer gas composition.

With the increase in temperature, using a bed of alumina particles, there was a tendency to decrease the CO content in the producer gas from about 48 to 45 vol% while, when using dolomite as a catalytic bed, substantially lower values of CO concentration were registered (13 vol%).

Regarding the concentration of H_2 in the producer gas, it was found that, with the increase in temperature and using alumina, the average H_2 concentration increases from 34 to 37 vol% and that the use of dolomite as a catalyst promoted an increase in H_2 concentration values in the range of 48–47 vol%.

Concerning the concentration of CO_2 in the producer gas, there was also a large difference in results between the two bed materials tested. Using alumina, the recorded CO_2 concentrations were in the range of 5–6 vol% and when dolomite was used a substantial increase in this concentration was observed. In this case, with the increase in temperature, there was a slight decrease from 30 to 27 vol% of the mean CO_2 concentration.

For the temperatures tested, no significant differences were observed in the concentration of CH_4 between the tests with dolomite and with alumina. The average values ranged from 10 to 12 vol%.

The results show that the composition of the producer gas is strongly dependent on the material of the particle bed. Using dolomite as a catalyst, a producer gas rich in H_2 and CO_2 was obtained, as indicated in several studies [5,8,9,15]. When using a bed of alumina particles, it was observed that CO was the predominant component followed by H_2, as reported by Andrés et al. [16].

This behavior is indicative that dolomite appears to be a suitable material to promote the destruction of tars by its action as a catalyst for tars reform reactions (8, 9), resulting in the promotion of the water gas shift reaction (1) as well. As a result of the higher level of H_2 and lower level in CO in producer gas, a large increase in the average value of the H_2/CO ratio was observed in the presence of dolomite (Fig. 3).

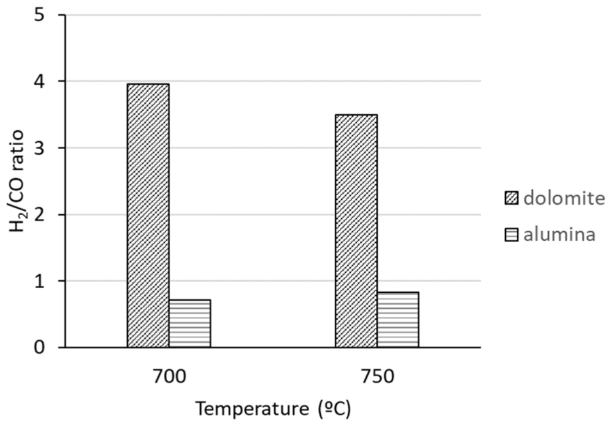

Fig. 3. Effect of bed material on H_2/CO ratio.

4. Conclusion

The catalytic co-gasification of glycerol/fat mixtures was studied using steam as a gasification agent. The results showed that dolomite is more effective than alumina in reducing the tar content of the producer gas. In the tested range temperatures, it was also found that the use of dolomite promotes the production of a producer gas rich in H_2 (47–48 vol%) and CO_2 (27–30 vol%) and with a mass ratio of H_2/CO between 3.5 to 4, which gives the gas more suitable properties for its use in combustion engines and in chemical synthesis for biofuels production, than the gas produced using alumina.

CRediT authorship contribution statement

Amaro Cruz: Experimental investigation, Formal analysis, Validation. **Elisa Ramalho:** Writing – review & editing. **Albina Ribeiro:** Writing – review & editing. **Rosa Pilão:** Conceptualization, Supervision, Original draft preparation, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Sutton DFavid, Brian Kelleher, Ross Julian. Review of literature on catalysts for biomass gasification. Fuel Process Technol 2001;73(3):155–73.

[2] Tan Ru, Tu Abdullah, Saiful Mahmud, Rohaya Zin, Khairuddin Isa. Catalytic steam reforming of complex gasified biomass tar model toward hydrogen over dolomite promoted nickel catalyst. Int J Hydrog Energy 2019;44:21303–14.

[3] Islam Md Waiul. A review of dolomite catalyst for biomass gasification tar removal. Fuel 2020;267:177095.

[4] Shanmuganandam K, Thanikaikarasan S, Anichai J. Application of dolomite for tar mitigation in downdraft gasifier: an experimental analysis. Mater Today Proc 2020;33:3537–9.

[5] Delgado Jesús, Maria P Aznar, José Corella. Biomass gasification with steam in fluidized bed: effectiveness of CaO, MgO, and CaO-MgO for hot raw gas cleaning industry and engineering chemical. Res Res 1997;36(5):1535–43.

[6] Peréz Pascual, Aznar María-Pilar, Miguel Caballero, Javier Gil, José Martín, José Corella. Hot gas cleaning and upgrading with a calcined dolomite located downstream a biomass fluidized bed gasifier operating with steam-oxygen mixtures. Energy Fuel 1997;11(6):1194-12031194-1203.
[7] Gil Javier, Miguel A Caballero, Juan A Martín, María-Pilar Aznar, Jose Corella. Biomass gasification with air in a fluidized bed: Effect of the in-bed use of dolomite under different operation conditions. Ind Eng Chem Res 1999;38:4226–35.
[8] Andrés João Manuel, Adolfo Narros, Rodríguez Hurtado, María Encarnación. Behaviour of dolomite, olivine and alumina as primary catalysts in air-steam gasification of sewage sludge. Fuel 2011;90(2):521–7.
[9] Pinto Filomen, Paula Marques, Mata R, Paula Costa, Francisco Gírio. Gasificação de biomassa rica em ligninha para produção de gás para usar em fermentação bacteriana CIES 2020 – XVII congresso iberico y XIII congresso iberoamericano de energia solar. 2020.
[10] Basu Prabir. Biomass gasification, pyrolysis and torrefaction: practical design and theory. 3rd ed.. Elsevier; 2018.
[11] Leal AL, Miguel Angel Soria, Luís Miguel Madeira. Autothermal reforming of impure glycerol for H2 production: Thermodynamic study including in situ CO2 and/or H2 separation. Int J Hydrog Energy 2016;41(4):2607–20.
[12] Meng Xiangmei. Biomass gasification: the understanding of sulfur, tar, and char reaction in fluidized bed gasifiers (Ph.D. thesis), Delft University of Technology; 2012.
[13] Almeida Ana, Rosa Pilão, Albina Ribeiro, Elisa Ramalho, Carlos Pinho. Co- gasification of crude glycerol/animal fat mixtures. Energyes 2020;13(7):1699.
[14] Hervya Maxime, Roberto Olcese, Mohammed M Bettahar, Martine Mallet, Renard Aurélien, Libeth Maldonado, et al. Evolution of dolomite composition and reactivity during biomass gasification. Appl Catal A Gen 2019;572:97–106.
[15] Vassilatos V, Georgios Taralas, Sjöström K, Emilia Björnbom. Catalytic cracking of tar in biomass pyrolysis gas in the presence of calcined dolomite. Canad J Chem Eng 1992;70(5):1008.
[16] Andrés Manuel, Adolfo Narros, Rodríguez Hurtado, María Encarnación. Air-steam gasification of sewage sludge in a bubbling bed reactor: Effect of alumina as a primary catalyst. Fuel Process Technol 2011;92:433–40.