Gasification of animal fat using dolomite as particle bed in a downdraft fixed bed reactor

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Abstract. One of the wastes generated in the tanning industry is hide fleshing, which contains 40 % of animal fat, currently being deposited in landfills. This work aims to study dolomite's catalytic capacity in gasifying this waste. The tests were carried out in a downflow fixed bed reactor using steam as a gasification agent and a bed of particles: alumina, dolomite and a mixture of these two materials. Tests were carried out at 750 ºC and 800 ºC, and the gas obtained was quantified and analyzed by gas chromatography. The results showed that dolomite improves the performance of the gasification process, with an increase in carbon and hydrogen conversion efficiencies, cold gas efficiency and dry gas yield. It was also possible to verify the catalytic capacity of this material in the cracking of hydrocarbons and its potential to promote the production of H_2. In addition, the mixed bed improved the results of the gasification parameters obtained at 800 ºC without compromising the degradation of the dolomite verified at higher temperatures.

Keywords: Animal fat, Gasification, Dolomite, Downdraft fixed bed reactor.

1 Introduction

The decrease in the use of fossil fuels, associated with an increase in environmental awareness, has promoted the growth in the use of renewable energy sources. Research on biomass as a renewable energy source has been increasing, contributing to the effort that has been made in the fight against climate change. In this perspective, the use of waste assumes an increasingly important role and can contribute to achieving the goal.

The leather industry generates a considerable amount of solid waste while processing hides and skins. Waste from the pre-fleshing process contains large amounts of fat and protein [1], which is currently sent to landfill [2]. The gasification of animal fat can be a way to sustain this waste.

Gasification is a useful thermochemical process for producing hydrogen, carbon monoxide, carbon dioxide, methane, and some hydrocarbons from carbon-containing feedstocks. The gas composition and heating value of producer gas determine its quality [3]. Producer gas has the potential to be a clean substitute for fossil fuels [4] and can either be used directly in engine/gas turbines and steam turbines to generate heat and electric power or further processed using the Fischer-Tropsch process to produce synthetic liquid fuels, which is of high commercial importance [5].

The main chemical reactions involved in the gasification process are illustrated in Table 1 [6].

Table 1. Summary of the chemical reactions in gasification.

Reaction type	Stoichiometric reaction equation	$\Delta H_{298,15k}$ (kJ/mol)	N°
Water-gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$	- 41.2	1
Boudouard reaction	$C + CO_2 \rightleftharpoons 2CO$	+ 172.58	2
Steam char reaction	$C + H_2O \rightleftharpoons CO + H_2$	+ 131	3
Methane steam reforming	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	+206	4
	$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$	+165	5
Methane dry reforming	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	+247	6
Thermal cracking	$pCnHx \longrightarrow qCnHy + rH_2$	+[200-300]	7
Tar steam reforming	$CnHx + nH_2O \longrightarrow (n + \frac{x}{2})H_2 + nCO$	+[200-300]	8
Tar dry reforming	$CnHx + nCO_2 \longrightarrow \frac{x}{2}H_2 + 2nCO$	+[200 – 300]	9
Tar carbon formation	$CnHx \longrightarrow \frac{x}{2}H_2 + nCO$	+[200 – 300]	10

Catalysts are considered a crucial component in the gasification process to maximize the hydrogen yield [7]. The effective transport of mass and heat between particles is facilitated by catalysts, promoting gasification reactions and contributing to the destruction of tars.

Natural and synthetic catalysts are two types utilized in the gasification process [8]. Dolomite and olivine are the most widely researched natural catalysts. Dolomite has the advantages of being cheap, effectively reducing tar content [9], and efficiently removing heavy hydrocarbons from the gas stream [8]. However, it has the disadvantage of susceptibility to attrition, which results in a loss of activity as a catalyst [10] and its rapid calcination in the gasifier, which can lead to the production of a gas with high levels of particles [11]. The tar removal capacity of dolomite is more active in the calcined form [12]. Calcined dolomite is obtained by removing CO_2 from $CaMg(CO_3)_2$ to get CaO and MgO [13]. The increased activity of calcined dolomite is mainly caused by CaO, which is known to be more active than MgO in tar-cracking reactions [14].

Cruz *et al.* [15] studied steam reforming of crude glycerol and animal fat mixtures using alumina or dolomite particles to evaluate the catalytic capacity of these minerals in removing tar from the producer gas. The results obtained showed that dolomite is more effective in reducing the tar content, evidencing its ability to catalyze the tar reform reactions and promote the water-gas shift reaction.

Inayat *et al.* [7] investigated the catalytic co-gasification of coconut shells and oil palm frond blends in the presence of cement, dolomite, and limestone. The results showed the most decisive influence of the process temperature on H_2 and CO yield and tar formation, followed by the catalyst loading and blending ratio. A catalyst loading of 30 wt % and process temperature of 900 °C were predicted as the optimized conditions for the reported co-gasification results. The highest H_2 yield of 20.64 vol % was obtained during catalytic co-gasification of the blended biomass with limestone, followed by cement (18.22 vol %) and dolomite (14.99 vol %).

González *et al.* [16] studied dolomite as a catalyst to improve tar removal and hydrogen production through a two-stage steam gasification process using olive cake. They found that the heavy hydrocarbons produced during steam gasification can be cracked using dolomite as a catalyst. Compared to uncatalyzed tests, it produces more gas with more hydrogen fractions, which can be attributed to the contributions of the steam reforming of hydrocarbon reactions and water gas shift reactions. They reported that dolomite is less efficient above 900 °C, probably due to the drop in activity at this temperature.

Valle *et al.* [17] investigated the dual catalyst-sorbent role of dolomite in the steam reforming of raw bio-oil. The results show that calcined dolomite is a feasible catalyst for producing H_2-rich syngas from raw bio-oil, with efficient CO_2 retention and a positive impact on the CO_2 global emissions balance.

Cao *et al.* [18] studied the potential of adding dolomite during the gasification of pine sawdust to improve the gasification characteristics, especially tar yield. The experiments were carried out at dolomite contents from 0 to 30 % by weight and gasification temperatures from 700 to 850 °C. They reported that the increase of dolomite used enhances the gas yield and tar elimination, and the increase in reaction temperature produces higher H_2 content and total gas yield, but it lowers the tar yield.

Shanmuganandam *et al.* [19] investigated the tar-cracking capability of dolomite in a downdraft gasifier. It was concluded that 700 °C was the optimum catalytic bed temperature, the optimum dolomite amount was 200 g, and the tar cracking effect of dolomite increased the calorific value of producer gas.

Zhang *et al.* [20] studied the effect of the operating conditions on gas composition, product distribution, and tar composition in the air-gasification of rice husks in the presence of dolomite. The results showed that increased temperature led to less tar formation and greater gas yield.

The present study intends to evaluate the catalytic effect of dolomite on the gas composition obtained from the gasification of animal fat and the impact on the gasification parameters.

2 Materials and methods

The animal fat used is solid at ambient temperature. Fat was characterized by its ultimate analysis and higher heating value (Table 2). In Fig 1. the fat thermogravimetric analysis is presented.

Table 2. Animal fat characterization.

Ultimate analysis (w/w% d.b)	Animal fat
Carbon	73.54
Hydrogen	11.75
Nitrogen	0.06
Ash	0.93
Oxygen (by diff)	13.72
HHV (kJ/g d.b)	37.48

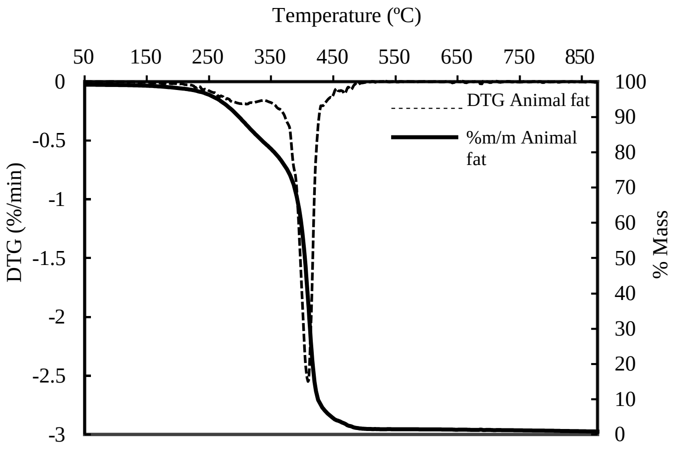

Fig. 1. TG and DTG curves for animal fat.

Fat is composed mainly of triglycerides, and when it is heated above 400 ºC, the carboxylic acids resulting from the primary cracking can follow two different routes of deoxygenation during the secondary cracking. The two routes occur simultaneously and will be favoured using catalysts [21]. Carbon dioxide and linear alkanes will be formed in the decarboxylation route, while water and alkenes will be formed in the decarbonization route.

The gasification of animal fat was studied in a downflow fixed bed reactor using steam as the gasification agent. The setup and test procedure are detailed and described by Almeida *et al.* [22]. In the study, an emulsion composed of 40 % (w/w) of fat and 60 % (w/w) of water was prepared and heated up to 36 ºC. This emulsion was fed to the reactor at a continuous mass flow rate between 2.22 and 2.30 g/min.

Tests were carried out at 750 ºC using particles of dolomite (2 to 5 mm in diameter) and alumina (6 mm in diameter) as a bed material to evaluate the catalytic effect of dolomite in the gasification process.

Dolomite ($MgCO_3CaCO_3$) is one of the primary catalysts most used in biomass gasification, and when it is calcined above 750 °C, it gives rise to the formation of MgO (21.3 %) and CaO (30.4 %) due to the loss of CO_2. One of the problems with its calcination is its dust reduction, which can cause operating problems and contamination of the gas produced with particles. This is a limitation of its use in gasification tests carried out at high temperatures using the experimental setup available. Information about the catalyst used can be consulted in a previous work [23].

Knowing that there is a longitudinal temperature stratification inside the reactor during gasification, tests were carried out with a set-point temperature of 800 ºC using a mixed bed of particles composed of 50 % by volume of dolomite particles and 50 % of alumina. The dolomite particles occupied the upper part of the reactor, where the temperature during the gasification test was lower, to minimize its calcination. The results obtained in this test were compared with the results obtained at 800 ºC using alumina as a particle bed.

The gasification parameters defined to evaluate the performance of the gasification process were carbon and hydrogen conversion efficiencies, dry gas yield, cold gas efficiency, and higher heating value determined according to [2]:

1) Carbon conversion efficiency (%):

$$\eta_c = \frac{MM_C \times A}{(Xc_{fat} \times \dot{m}_{fat})} \tag{11}$$

where A is the total molar flow (kmol/s) of carbon-bearing components (CO_2, CO, CH_4, C_2H_4, and C_2H_6) present in the producer gas, MM_c the molar mass of carbon (kg/kmol), xc_{fat} the carbon mass fraction (kg/kg *d.b.*) in fat, and $\dot{m}_{fat}$ the mass feed flow rate of fat (kg/s *d.b.*).

2) Hydrogen conversion efficiency (%):

$$\eta H = \frac{MM_H \times B}{x_{H_{fat}} \times \dot{m}_{fat}} \tag{12}$$

where B is the total molar flow (kmol/s) of hydrogen-bearing components (H_2, CH_4, C_2H_4, and C_2H_6) present in the producer gas, MM_H is the hydrogen molar mass (kg/kmol), and x_{Hfat} is the hydrogen mass fraction (kg/kg *d.b.*) of fat.

3) Dry gas yield (Nm^3/kg):

$$Y = \frac{V_g}{\dot{m}_{fat}} \tag{13}$$

where V_g is the volumetric flow rate (Nm^3/s) of producer gas.

4) Cold gas efficiency (%):

$$\eta g = \frac{V_g \times HHV_g}{\dot{m}_{fat} \times HHV_{fat}} \tag{14}$$

where HHV_g is the producer gas higher heating value (kJ/m^3), and HHV_{fat} the higher heating value (kJ/kg *d.b.*) of fat.

5) Higher heating value of producer gas (kJ/m^3):

$$HHV_g = y_{H_2}\, x\, HHV_{H_2} + y_{CO}\, x\, HHV_{CO} + y_{CH_4}\, x\, HHV_{CH_4} + y_{C_2H_4}\, x\, HHV_{C_2H_4} + y_{C_2H_6}\, x\, HHV_{C_2H_6} \tag{15}$$

where y_i is the volumetric fraction (%) of the component in the producer gas, and HHV_i its higher heating value (kJ/m^3).

3 Results and discussion

The use of dolomite as a catalyst in the fat gasification process was studied at 750 ºC, using a particle bed composed only of dolomite, and at 800 ºC using a mixed particle bed (50 % dolomite and 50 % alumina). The results obtained under these two conditions were compared with those obtained in tests carried out at 750 ºC and 800 ºC, with a bed of alumina particles. Fig. 2 shows the amounts obtained from each compound in the gas per kg of fat gasified.

The gas obtained is composed of hydrogen, carbon monoxide, methane, carbon dioxide, ethylene, and ethane, and the data show that the obtained amount of each compound depends on the composition of the particle bed.

Comparing the results obtained at 750 ºC using alumina and dolomite as a bed of particles, it is possible to verify that per kg of gasified fat, the volumetric amounts of H_2 and CO_2 produced increase by 50 %, the amount of CH_4 increases by 16 % and that of C_2H_4 reduces by about 18 %. This change in the composition may result from combined actions between the possible alteration of the route followed in the secondary cracking of fat and the catalytic activity of cracking of tar attributed to this material.

This evolution trend is also observed when comparing the results obtained at 800 ºC with a mixed bed with the results obtained at the same temperature using alumina. However, no significant differences were observed in the values obtained for H_2, CH_4 and C_2H_6, the most significant difference being the 80 % increase in CO_2 production. The mixed bed has only 50 % of dolomite placed in the lowest temperature zone of the reactor. Therefore, a smaller impact on the results obtained for the gas composition would be expected.

Regarding the volume of CO produced per kg of gasified fat, a reduction of about 50% was observed in its value in tests carried out at 750 ºC using dolomite. This trend was reversed entirely in the tests carried out at 800 ºC, registering an exponential increase in the volume of CO produced with the addition of dolomite to the bed of particles. This behavior results from the chemical kinetics followed under these test conditions.

Table 3 shows the values obtained for the gasification parameters under study for the tested test conditions. The analysis of the results shows that using dolomite as a bed of particles increases the efficiency of hydrogen and carbon conversion efficiencies, cold gas efficiency, and dry gas yield. The improvement of these parameters is associated with the increase in the gas phase yield promoted by dolomite and the catalytic action of this material on hydrocarbon cracking reactions.

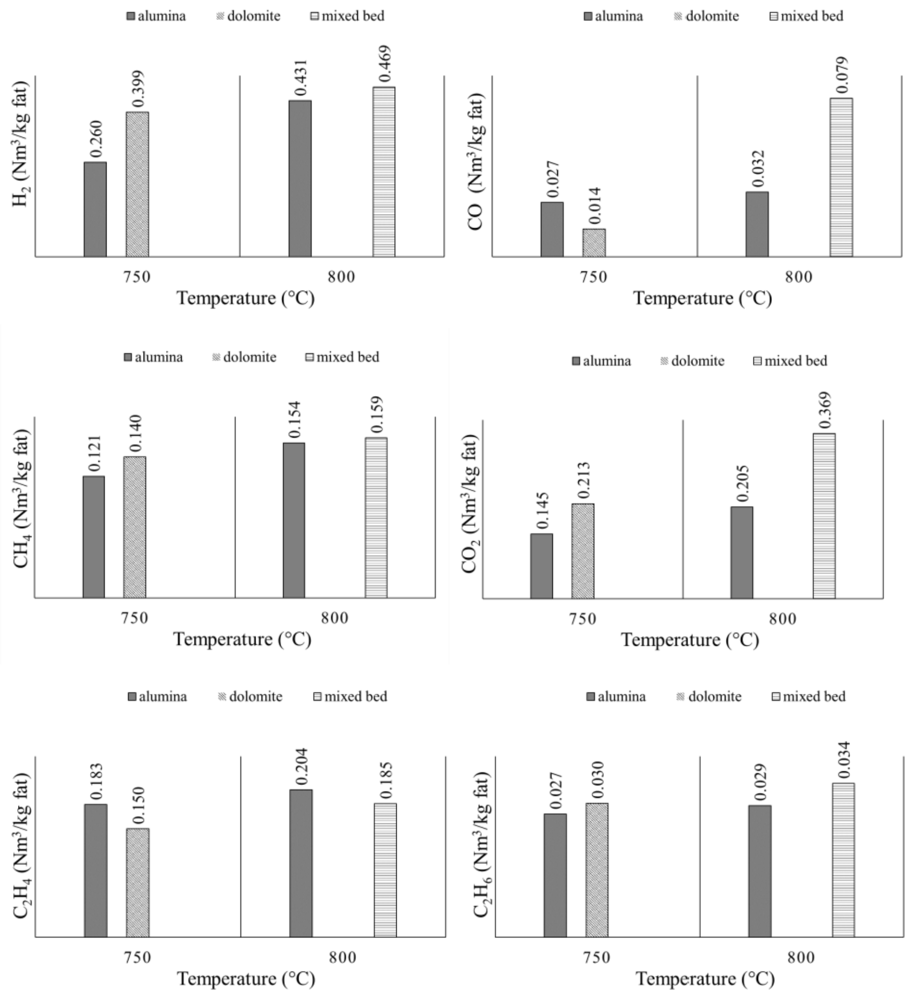

Fig.2. Effect of bed particle composition on producer gas obtained.

Table 3. Effect of bed particle composition on gasification parameters.

Gasification parameters	750ºC		800ºC	
	Alumina	Dolomite	Alumina	Mixed bed
Carbon conversion (%)	51.9	52.8	62.3	76.1
Hydrogen conversion (%)	72.9	82.0	94.5	96.5
Cold gas efficiency (%)	59.0	60.1	72.2	73.4
Dry Gas Yield (m^3/kg dry fat)	0.8	1.0	0.9	1.2
HHVg (MJ/m^3)	28.8	24.2	26.3	22.5

The decrease in higher heating value when using dolomite is related to the change in the volumetric composition of the producer gas, with the decrease in the concentration of C_2H_4 being the main factor.

Using the mixed bed allowed for improving the results of the gasification parameters obtained at 800 ºC with alumina without compromising the degradation of the dolomite. The maximum values obtained were 76.1 % and 96.5 % for carbon and hydrogen conversion efficiencies, 73.4 % for cold gas efficiency, 1.2 m^3/kg for dry gas yield and 22.5 MJ/m^3 for HHVg.

4 Conclusions

The gasification of animal fat was studied in a fixed bed reactor using particles of alumina, dolomite and a mixture of the two materials. The results obtained showed that the use of dolomite as a bed of particles results in an increase in the produced volume of H_2 and CO_2 and a reduction in the volume of C_2H_4 per unit mass of gasified fat when comparing the results with those obtained using alumina as particle bed. The registered change in composition resulted in a reduction in the HHV of the gas. Regarding the remaining gasification parameters, an increase in their values was observed. Using a mixed bed of particles composed of 50 (Vol %) of each material improved the performance of the fat gasification process at 800 ºC, overcoming the problem of calcining dolomite at high temperatures.

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