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# Simulation of the gasification of animal wastes in a dual gasifier using Aspen Plus<sup>®</sup>



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# ABSTRACT

The gasification of an animal waste biomass (manure) in a dual gasifier was studied using the software Aspen Plus<sup>®</sup>. For this purpose, a model based on a Gibbs free energy reactor was considered. Effects of the gasification temperature, the gasifying/biomass ratio and the use of steam and CO<sub>2</sub> as the gasifying agents on the composition and the low heating value (LHV) of the produced syngas were evaluated. In this sense, the H<sub>2</sub>/CO ratio and the LHV were the parameters calculated to stablish the best operating conditions for the production of either hydrocarbons via Fischer-Tropsch or energy. Furthermore, the CO<sub>2</sub> net emissions generated by the gasification process were also important in the selection of the best operating conditions from an environmental point of view. The obtained results showed that for both gasifying agents the  $H_2$  and CO production was favoured at high temperatures whereas the production of  $CH_4$  and  $CO_2$ was favoured at low ones. On the other hand, the H<sub>2</sub> production was higher when steam was used as the gasifying agent and the formation of CO was enhanced when CO<sub>2</sub> was considered as gasification agent. An increase of the gasifying agent/biomass ratio had a negatively influence on the production of CH<sub>4</sub>, leading to a decrease of the LHV. Therefore, steam as the gasifying agent and high temperatures favoured the obtaining of a syngas suitable for the Fischer-Tropsch process whereas CO<sub>2</sub> and low gasification temperatures enhanced a syngas with a high LHV which could be used for energy production. Finally, the net  $CO_2$  emissions were estimated to be lower when  $CO_2$  was again used as the gasifying agent.

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# 1. Introduction

Due to the population growth, the world energy demand has been exponentially increasing during the last years. This energy demand is one of the main causes of the depletion of fossil fuel reserves. Moreover, it is well known that the use of fossil fuels has been associated to some environmental problems such as CO<sub>2</sub> emissions, which is considered as the main greenhouse gas that contributes to the global warming. In addition, the emission of NOx and SOx can result in acid rain [1]. In this regard, biomass seems to be the most viable route for the bioenergy production. Among the different type of biomass, animal wastes or manure has been associated to some hygienic and environmental problems such as subterranean and surface water, ground and air contamination, odors and greenhouse gases and ammonia emissions [2]. In this sense, manure has been traditionally used as fertilizer and landfills [3]. However, landfills require large amounts of land [4]. Besides, the use of manure biomass as fertilizer needs to be

\* Corresponding author. *E-mail address:* marialuz.sanchez@uclm.es (L. Sanchez-Silva). handled due to the strict regulation and to avoid land saturation with phosphorus [4,5]. Therefore, the use of animal waste or manure as a feedstock for bioenergy production seems to be a very good alternative [6].

Generally, the conversion of biomass into either fuels or energy can be mainly carried out through biological and thermochemical processes. During biological processes, biomass is converted into biogas and residual digested by the action of living organism. On the other hand, in thermochemical processes, biomass is transformed into biofuels, gases and chemicals by applying heat and pressure [7]. Gasification is one of the most important thermochemical process due to the overall plant efficiencies can be increased using the produced syngas in electricity production system, such as gas engines, gas turbines and fuels cells [4]. Biomass gasification can be defined as the conversion of biomass into a gaseous fuel by heating in a partial oxidation atmosphere. The first step of the gasification process is the pyrolysis process when the volatiles are released and the char is formed [8]. After this primary step, the char reacts with the gasifying agent to produce mainly carbon dioxide, carbon monoxide, hydrogen and methane. The composition of the obtained gas fuel depends on both the gasifying agent used and the temperature and the type of biomass. In this sense, steam gasification has attracted more interest as a higher hydrogen yield can be reached [7].

The configuration of the gasifier is also a key parameter for the optimization of the gasification process. Moving/fixed bed and fluidized bed are the two main types of gasifier. Fixed bed reactors are only suitable for small scale. On the other hand, fluidized bed offers a high fuel flexibility and a better mass and energy transfer than moving bed gasifiers. A subcategory of these ones is the dual fluidized bed gasifiers which are currently being under development [9]. This kind of reactor consists of the separation of the gasification and combustion zones to obtain a high quality gas. Part of the char is burnt in the combustion zone increasing the temperature of the bed particles, whereas in the gasification zone the biomass is gasified with the corresponding gasifying agent generating a  $N_2$ -free fuel gas [10]. The hot particles coming from the combustion zone are returned to the gasification zone providing the necessary heat for the reaction [9].

Furthermore, for the process scale up, a depth investigation of the plant behaviour and the operating conditions is required. In this regard, the simulation of the process seems to be a good option for the preliminary estimation of the process behaviour without requiring pilot plants acquisition and the temporal and financial efforts associated to it [4]. In this work, the commercial software Aspen  $\operatorname{Plus}^{\circledast}$  was used to simulate the gasification of one dairy manure sample. The simulation of coal gasification by using Aspen Plus<sup>®</sup> has been reported by many authors [11–13]. Although the simulation of biomass gasification is also present in literature, there are few studies that report the simulation of manure gasification. Im-orb et al. [14] developed the parametric analysis of two rice straw gasification processes using a thermodynamic model-based approach developed in Aspen Plus<sup>®</sup>. They reported the possibility of one step H<sub>2</sub>/CO ratio adjustment in a gasifier at thermal self-sufficient condition. Beheshti et al. [15] simulated the air-steam gasification of biomass for hydrogen and syngas production by using the Aspen Plus<sup>®</sup> simulator together with FORTRAN subroutines. The simulation results showed that high temperatures promote the production of useful syngas and hydrogen yield. They also validated the model with experimental data. Adeyemi and Janajreh [16] used a kinetic-based Aspen Plus® model for the simulation of the gasification of Kentucky coal and wood waste in an entrained flow gasifier. An increase in the diameter and height sizes lead to a rise in the CO and H<sub>2</sub> mole fraction, showing an opposite trend for the CO<sub>2</sub> and H<sub>2</sub>O composition. Doherty et al. [9] developed an equilibrium model to simulate the gasification of woody biomass in a dual fluidised bed gasifier. The model was based on Gibbs free energy minimization and predicted the operating parameters in good agreement with reported data. Hammer et al. [17] used an Aspen Plus<sup>®</sup> model to design a pyrolysis process for the production and utilization of pyrolytic oil from equine waste. A dual fluidized bed combustion reduction integrated pyrolysis system was identified as the pyrolytic oil production.

The aim of the present work was to evaluate the gasification process of manure using the software Aspen Plus<sup>®</sup>. The combination of different operating conditions, such as the temperature and the gasifying agent (steam and/or  $CO_2$  in this case) were studied to stablish the best ones for the production of either chemicals via Fischer-Tropsch or energy. Moreover, the  $CO_2$  net emissions generated during the gasification process were calculated, being also this parameter important in the selection of the best operating conditions from an environmental point of view.

# 2. Materials and methods

In this section, the modelling approach of the gasification process for a manure sample, including the process assumptions, the block diagram and the description of the different blocks used in the software Aspen Plus<sup>®</sup> is presented.

# 2.1. Biomass sample

The biomass studied was a dry dairy manure sample from the province of Québec (Canada). The manure sample was first stored in a tank to remove part of its moisture and then dry in a stove at 105 °C. Physico-chemical characterization of this sample, including proximate and ultimate analyses, the content of metals, cyanide ( $CN^-$ ), chloride ( $CI^-$ ) and the calorific value are shown in Table 1.

# 2.2. Process assumptions

There are some assumptions considered in the simulation of the manure gasification process [18,19]: (i) gases evolved during gasification were H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S and HCl; (ii) char is only composed of carbon and ash; (iii) ash is considered to be inert and does not participate in the reactions; (iv) 100% of char conversion during gasification, (v) all reactions involved in the gasification process reach the equilibrium and (vi) the reactions involved are summarized below [3,10]:

Pyrolysis	$Biomass_{(s)} \rightarrow$	Volatile matter <sub>(g</sub>	$) + Char_{(s)} +$	- Ash <sub>(s)</sub>	(1)	)
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Boudouard reaction  $C_{(s)} + CO_{2_{(g)}} \Leftrightarrow 2CO_{(g)}$  (2)

Metanation  $C_{(s)} + 2H_{2_{(g)}} \hookrightarrow CH_{4_{(g)}}$  (3)

Steam gasification  $C_{(s)} + H_2O_{(g)} \hookrightarrow CO_{(g)} + H_{2_{(g)}}$  (4)

Watergas - shift 
$$CO_{(g)} + H_2O_{(g)} \hookrightarrow CO_{2(g)} + H_{2(g)}$$
 (5)

Steam methane reforming  $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2_{(g)}}$  (6)

Hydrogen sulfide formation 
$$H_{2(g)} + S_{(s)} \rightarrow H_2S_{(g)}$$
 (7)

Ammonia formation 
$$0.5N_{2(g)} + 1.5H_{2(g)} \rightarrow NH_{3_{(g)}}$$
 (8)

Hydrochloric acid formation 
$$Cl_{2(g)} + H_{2(g)} \rightarrow 2HCl_{(g)}$$
 (9)

### Table 1

Ultimate analysis (wt.%)daf <sup>a</sup>					Proximate analysis (wt.%) <sup>a</sup>					HHV	(MJ/kg)	
С	Н		N	S	0	М		Ash	VM	FC		
51.43	6.72		1.74	0.52	39.59	3.45		20.78	64.09	11.68	18.4	
Mineral o	content (ppm)											
Al	Ca	Cr	Cu	Fe	К	Mg	Na	Ni	Р	Si	Cl⁻	CN⁻
516	16,997	73	-	3800	5806	6426	37,445	-	16,207	537	42,866	45

<sup>a</sup> daf = Dry and ash free basis; M = Moisture; VM = Volatile matter; FC = Fixed carbon; HHV = High heating value.

Table 2					
Blocks description	used	in	the	simulation	model.

Block name	Aspen Plus® name	Description
DECOMPOS	RYIELD	Biomass pyrolysis reactor based on the conversion of the non-conventional biomass into conventional components using a calculator block
CHARSEP	SEP2	Separator of the amount of char necessary to reach the gasification temperature through its combustion
COMBUST	RSTOIC	Char combustion reactor based on the stoichiometry of the combustion reaction
NSCL	RSTOIC	Reactor used to simulate the NH <sub>3</sub> , HCl and H <sub>2</sub> S during the gasification process
GASSEP	SEP2	Separator of the NH <sub>3</sub> , HCl and H <sub>2</sub> S
GASIF1	RGIBBS	Biomass char gasifier based on equilibrium models that minimizes the free energy Gibbs
GASIF2	RGIBBS	Gasifier at which the output composition gas is adjusted
GASMIX	MIXER	Blending of gasifier output with $NH_3$ , HCl and $H_2S$

# 2.3. Gasification process modelling with Aspen Plus<sup>®</sup>

According to Beheshti et al. [15], there are two different ways to model the gasification process in Aspen Plus<sup>®</sup> which consider either the complete equilibrium of the process or the corresponding kinetic mechanism. In this work, an equilibrium model based on a Gibbs free energy minimization was used to simulate a dual fluidized bed gasifier [20] for the conversion of manure into syngas. In this kind of reactors, the gasification and the combustion zones are separated. Fig. 1 shows the flowsheet diagram in Aspen Plus<sup>®</sup> of the simulation whereas Table 2 lists a brief explanation of the blocks used.

Biomass is defined as a non-conventional component in the simulation, its chemical composition was evaluated through the ultimate and proximate analyses and its high heating value (HHV), all of them experimentally obtained and shown in Table 1. HCOALGEN was the model selected for the enthalpy calculation and the equation of state used to estimate the physical properties of the conventional components was Peng-Robinson with Boston-Mathias function, being the appropriate for high temperature gasification processes [21,22].

The stream BIOMASS, with a mass flow of 100 kg/h, was fed to the reactor DECOMPOS to simulate the biomass pyrolysis reactor based on the conversion of the non-conventional biomass into conventional components. All the obtained char in this reactor was supposed to be 100% carbon. Subsequently, the amount of the char which should be burnt in the combustion zone (COMBUST) to increase the temperature of the bed particles, providing the necessary heat for the reaction, was split in CHARSEP using a design specification. Furthermore, the air flow was calculated using a calculator block and taking into account an air excess of 1.12 regarding the char burnt in the combustion chamber. The rest of the stream was then fed into NSCL to simulate the conversion of the nitrogen, chlorine and sulfur contained in the biomass into NH<sub>3</sub>, HCl and H<sub>2</sub>S, respectively. These gaseous compounds were split in GASSEP from the main stream, which was fed into GASIF1. The aim of this block was to simulate the reaction between the biomass char and the gasifying agent which was introduced into the reactor at 1 bar and 150 °C. The stream QCOMB was supposed to be the energy (in the form of heat particles) which was transferred from the combustion chamber to the gasification one. Blocks DECOMPOS and NSCL were energetically integrated with GASIF1 by streams ODECOMP and ONSCL.

As thermodynamic equilibrium models underestimate  $CO_2$  and  $CH_4$  formation and overestimate  $H_2$  and CO formation [21], block GASIF2 was used to adjust the gas composition. In this sense, the equilibrium temperatures of Reactions (5) and (6) were limited to 300 °C above the gasification temperature and 335 °C below the gasification temperature, respectively. In addition, the equilibrium reactions were also specified.

Finally, the effluent from GASFI2 was mixed with that of GAS-SEP in GASMIX to obtain the final output syngas from the manure gasification process.



Fig. 1. Aspen Plus® flowsheet simulation of the gasification process.

In this work, the influence of three gasification temperatures (750, 850 and 950 °C), two gasifying agents (steam and CO<sub>2</sub>) and different gasifying agent/biomass ratios (from 0.1 to 2.1) on the composition and the low heating value (LHV) of the syngas obtained were evaluated. In this sense, the H<sub>2</sub>/CO ratio and the LHV were the parameters calculated to stablish the best operating conditions for the production of either hydrocarbons via Fischer-Tropsch, with a H<sub>2</sub>/CO  $\approx$  2, or energy (syngas with a high LHV). The LHV of the gas produced (LHV<sub>gas</sub>) was calculated by Eq. (1) [1]:

$$LHV_{gas} = 10.8 * y_{H_2} + 12.6 * y_{CO} + 35.8 * y_{CH_4}$$
(1)

where  $y_i$  is the molar fraction of each gas compound (H<sub>2</sub>, CO and CH<sub>4</sub>).

# 3. Results

# 3.1. Model validation

To validate and check the accuracy of the designed simulation process, the dual gasifier of a real plant in Güssing (Austria) was

# Table 3

Syngas composition (% vol. dry basis) obtained with the simulation model and Güssing plant.

Compound	Model composition	Güssing plant
H <sub>2</sub>	50	35-45
CO	17	22-25
CH <sub>4</sub>	11	$\sim 10$
$CO_2$	22	20-25

considered. In this plant, the gasification of biomass chips with steam at 850 °C is carried out. The scheme of the real plant is reported elsewhere [23–25]. A general biomass composition of chips was used in this validation. The syngas composition obtained in this plant was reported elsewhere [26]. Table 3 compares the composition of this syngas obtained from Güssing plant to that computed by the simulation model, both obtained using the same operating conditions: steam as the gasifying agent and a gasification temperature of 850 °C at atmospheric pressure. A good agreement was obtained despite errors of 5% and 7% in the estimation of the composition of H<sub>2</sub> and CO, respectively. Therefore, the simulation model can be considered valid to describe a gasification process.

# 3.2. Influence of the gasification temperature, gasifying agent and gasifying agent/biomass ratio

The influence of the operating conditions on both the composition and the low heating value (LHV) of the syngas produced (for LHV calculation only  $H_2$ , CO and  $CH_4$  are considered) are discussed in this section.

Figs. 2 and 3 show the evolution of the main gases evolved, namely  $H_2$ , CO, CO<sub>2</sub> and CH<sub>4</sub> [27], during the manure gasification process at the three gasification temperatures studied (750, 850 and 950 °C) and at different gasifying agent/biomass ratios using steam and CO<sub>2</sub> as the gasifying agents, respectively. Furthermore, the evolution of LHV with the gasifying agent/biomass ratio at the three temperatures studied is shown in Fig. 4.

Figs. 2 and 3 show that  $H_2$  and CO production increased when the gasification temperature also increased whereas the produc-



Fig. 2. Syngas composition (dry basis) obtained for the steam gasification of manure at three different temperatures.



Fig. 3. Syngas composition (dry basis) obtained for the CO<sub>2</sub> gasification of manure at three different temperatures.



Fig. 4. LHV evolution with the gasifying agent/biomass ratio at different temperatures and gasifying agents.

tion of  $CH_4$  and  $CO_2$  was favoured at low temperatures for both gasifying agents. This fact was explained by the Bouduard and the steam gasification endothermic reactions (Reactions (2) and (4), respectively) which was favoured at high temperatures. In this type of reactions and accordingly to Le Chatelier's principle, the higher the temperature, the higher the products production observed. Another reaction which should be taken into account is the water gas shift reaction (Reaction (5)). Higher temperatures favour the CO production, decreasing the H<sub>2</sub> and CO<sub>2</sub> amounts in the produced syngas. However, this reaction is an equilibrium, thus, the formed products depends on the amount of steam and  $CO_2$  which is present in the gasifying medium. On the other hand, the decrease in CH<sub>4</sub> concentration was explained by the occurrence of the methane reforming reaction (Reaction (6)), being also endothermic and favoured at high temperatures [15].

The higher H<sub>2</sub> production was favoured by the temperature and high gasifying agent/biomass ratio when steam was used as gasifying agent (Fig. 2) [5] because H<sub>2</sub> is produced in all the reactions where steam is involved (Reactions (4)(6)). However, the H<sub>2</sub> production during the CO<sub>2</sub> gasification decreased at 850 and 950 °C (Fig. 3) which could be attributed to the occurrence of the reverse waster gas shift reaction enhanced by the increase of the CO<sub>2</sub> concentration.

The production of  $CH_4$  was also improved when steam was used as the gasifying agent. However, at 950 °C it was hindered because the occurrence of the methane reforming reaction [15]. For both atmospheres studied,  $CH_4$  production decreased when the gasifying agent/biomass ratio increased.

The maximum CO generation was obtained when  $CO_2$  was used as the gasifying agent [28] due to the Bouduard reaction (Reaction (2)) ant its production was kept almost constant for ratios higher than 0.5 at 750 °C. Besides, its production was almost constant at 850 °C and passed through a maximum at 950 °C for a ratio of 0.9. On the other hand, CO production decreased when steam was used as the gasifying agent due to the consumption of the formed CO through the WGS reaction [22].

Regarding  $CO_2$  production, it is obvious that more  $CO_2$  was found in the outlet stream during the gasification with  $CO_2$  due to it could be only consumed through the Bouduard and the



Fig. 5. Net CO $_2$  emissions for manure steam and CO $_2$  gasification at 750, 850 and 950  $^\circ\text{C}.$ 

reverse WGS reactions, which are favoured at high temperatures. On the contrary, the production of  $CO_2$  increased when the steam/biomass ratio increased due to the occurrence of the water gas shift reaction.

Fig. 4 shows the evolution of the low heating value (LHV) of the produced syngas at the three considered temperatures.  $CH_4$  is the main contributor to the LHV of syngas [1]. As expected, this parameter followed the same decreasing trend for increasing temperatures.

The highest value of LHV of the syngas was obtained when  $CO_2$  was used as the gasifying agent and favoured at low gasifying agent/biomass ratios. As above mentioned, the maximum CO production was obtained by this agent. The amount of generated CH<sub>4</sub> with both gasifying atmospheres was almost the same. Consequently, LHV values were higher when  $CO_2$  was used as the gasifying agent due to the CO is the second contributor to LHV [1].

# 3.3. Net CO<sub>2</sub> emissions

The net  $CO_2$  emissions per kg of feeding biomass were also calculated considering the sum of the  $CO_2$  generated in the combustion chamber and the  $CO_2$  concentration of the produced syngas (as positive contribution) and the  $CO_2$  used as gasifying agent (as negative one). Their evolution with the gasifying agent/biomass ratio is shown in Fig. 5.  $CO_2$  emissions in both the combustion and the gasification chambers (considered as a positive contribution to the emissions) along with the  $CO_2$  used as the gasifying agent (considered as a negative contribution to the emissions) have been considered in this calculation.

In the case of using steam, the  $CO_2$  net emissions increased when increasing gasifying agent/biomass ratios; similar trend is observed in Fig. 2. For ratio values up to 0.9, the  $CO_2$  net emissions were lower at higher temperature, which could be attributed to the occurrence of WGS reaction at these conditions. Nevertheless, from a ratio equal to 0.9, the  $CO_2$  generated in the combustion chamber directly affected the net emissions calculation. On the other hand, when  $CO_2$  was used as the gasifying agent the net emissions decreased with increasing values of the gasifying agent/biomass ratios due to the occurrence of the Bouduard reaction. At 750 °C, an increase in the net emission up to a ratio of 0.5 was observed. At low temperatures and concentrations, the Bouduard reaction was not favoured.

# 3.4. Uses of the produced syngas

The H<sub>2</sub>/CO molar ratio of the produced syngas defines its further use. Thus, it could be used, for example, in the synthesis of hydrocarbons via Fischer-Tropsch (FT) or as a gas fuel. Specifically, a syngas with a value of the H<sub>2</sub>/CO ratio close to 2 can be used in the FT synthesis.

Table 4 shows the simulation cases leading to a value of the  $H_2/CO$  molar ratio close to 2 together with the corresponding ratio gasifying agent/biomass used and the generated net  $CO_2$  emissions.

Syngas obtained by steam gasification at 850 °C with a gasifying agent/biomass ratio of 0.7 was considered the most suitable one for the FT process (Fig. 5). Although the net CO<sub>2</sub> emission value was not the lowest one (the temperature of 950 °C presented the lowest value among the cases at which steam was used as gasifying agent), the H<sub>2</sub>/CO ratio was the closest to 2. Furthermore, low temperature implies less energy to be provided by the combustion chamber to the gasification chamber, leading more available char to be gasified. On the other hand, the highest values of the LHV were obtained when the CO<sub>2</sub> was used as the gasifying agent (Fig. 4). Thus, the gasification process of manure at 750 °C using CO<sub>2</sub> as the gasifying agent and a gasifying agent/biomass ratio of 0.1 was the best option to obtain a gas fuel with a LHV value of 18.2 MJ/N m<sup>3</sup>.

# 4. Conclusions

In this work, an equilibrium model based on the Gibbs free energy minimization was developed using Aspen Plus<sup>®</sup> for the study of manure gasification in a dual gasifier. Once the model was validated with experimental data found in literature, the influence of the gasification temperature, the use of steam and CO<sub>2</sub> as the gasifying agent and the gasifying agent/biomass ratio on the composition and the LHV of the syngas obtained from the manure gasification were studied. H<sub>2</sub>/CO ratio and the LHV were calculated to stablish the best operating conditions for the production of a syngas suitable for either hydrocarbons via Fischer-Tropsch (FT), with a  $H_2/CO$  ratio  $\approx 2$ , or energy. The obtained results showed that the syngas obtained by steam gasification at 850 °C with a gasifying agent/biomass ratio of 0.7 was considered the most suitable one for the FT process. On the other hand, the highest values of the LHV were obtained when the CO<sub>2</sub> was used as the gasifying agent. Therefore, the gasification process of manure at 750 °C using CO<sub>2</sub> as the gasifying agent and a gasifying agent/biomass ratio of 0.1 was the best option to obtain a gas fuel with a LHV value of 18.2 MJ/N m<sup>3</sup>. In both cases, the best operating conditions did not lead to the lowest net CO<sub>2</sub> emissions. For this reason, the simulation model here proposed allowed to develop other investigations about the improvement of the biomass gasification process such as the evaluation of mixtures of steam and CO<sub>2</sub> as the gasify-

Table 4							
Simulations	leading to a	$H_2/CO$	molar	ratio	close	to	2.

H <sub>2</sub> /CO	Gasifying agent	T (°C)	Gasifying agent/Biomass	Net CO <sub>2</sub> emissions
2.03	Steam	750	0.7	0.83
2.02	Steam	850	0.7	0.81
2.11	Steam	950	0.7	0.80

ing agent to obtain a syngas with a  $H_2/CO$  ratio suitable for the FT process and low net  $CO_2$  emissions.

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