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**DOI**

[10.1016/j.biombioe.2021.105982](https://doi.org/10.1016/j.biombioe.2021.105982)

**Publication date**

2021

**Document Version**

Final published version

**Published in**

Biomass and Bioenergy

**Citation (APA)**

Cavalli, A., Tetteroo, R., Graziadio, M., & Aravind, P. V. (2021). Catalytic reforming of acetic acid as main primary tar compound from biomass updraft gasifiers: screening of suitable catalysts and operating conditions. *Biomass and Bioenergy*, 146, Article 105982. <https://doi.org/10.1016/j.biombioe.2021.105982>

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# Catalytic reforming of acetic acid as main primary tar compound from biomass updraft gasifiers: screening of suitable catalysts and operating conditions

A. Cavalli<sup>a,\*</sup>, R. Tetteroo<sup>a</sup>, M. Graziadio<sup>b,c</sup>, P.V. Aravind<sup>a</sup>

<sup>a</sup> Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Delft, the Netherlands

<sup>b</sup> Engineering Faculty, University of Tuscia, Viterbo, Italy

<sup>c</sup> ENEA, Department of Energy Technologies, Rome, Italy

## ARTICLE INFO

### Keywords:

Biomass updraft gasifier  
Primary tar reforming  
Acetic acid  
Dolomite  
Olivine  
Metal-based catalyst

## ABSTRACT

Tar compounds have been defined as Achilles' heel in biomass gasification. Catalytic reforming solves problems caused by tar by converting them into H<sub>2</sub> and CO. Most of the research has focused on secondary and tertiary tar reforming while some information on primary tar can be derived from bio-oil reforming. However, these studies use humidified N<sub>2</sub>, Ar or He as gas carrier. Therefore, in this work, three catalysts are compared for reforming 40 g/Nm<sup>3</sup> acetic acid as main primary tar compound from biomass updraft gasification using simulated biosyngas as gas carrier. The catalysts were tested over a 72 h period between 680 and 750 °C with a gas composition of 35.0 vol% H<sub>2</sub>O, 2.3 vol% CO, 19.5 vol% CO<sub>2</sub>, 3.6 vol% CH<sub>4</sub>, 24.0 vol% H<sub>2</sub> and 15.6 vol% N<sub>2</sub>. Olivine completely converted acetic acid, but a considerable amount of carbonaceous deposits was found on the catalyst and the catalytic activity decreased over time with 0.2 g/Nm<sup>3</sup> hydroxyacetone measured in the last day of testing. Dolomite showed promising performances by completely converting acetic acid and accumulating carbonaceous deposits only in the low temperature part of the catalyst bed. The carbonaceous deposits could be suppressed increasing the steam content to 50.1 vol% and the temperature to 900 °C. However, the catalyst became excessively brittle. The metal-based catalyst out-performed the naturally-occurring catalysts by completely converting acetic acid with almost no carbonaceous deposits accumulation. These results are expected to help the further development of tar reformers, and the commercialisation of biomass updraft gasifiers based systems.

## 1. Introduction

Biomass gasification has attracted considerable attention as a technology to reduce environmental pollution and to face the steady increase in the world heat and power consumption. Gasification converts solid biomass into biosyngas, a gaseous mixture of hydrogen, carbon monoxide, methane, carbon dioxide, alongside nitrogen and water vapour, whose presence and concentrations are highly dependent on the gasification agent used. However, biosyngas also contains minor concentrations of species that might damage downstream equipment. These contaminants include nitrogen compounds (NH<sub>3</sub> and HCN), sulfur compounds (H<sub>2</sub>S), halides (HCl), particulate matter (carbon and solid metals), and tar (e.g., toluene and naphthalene). Among biosyngas contaminants, tar requires particular attention.

A common definition of tar is that of organic hydrocarbons with a

molecular weight (MW) higher than benzene [1]. Otherwise, Milne et al. defined tar as the organic compounds, largely aromatic, released during pyrolysis or gasification of any organic material [2]. The same authors developed a tar classification method based on the maturation of tar from their initial release during the pyrolysis step. The first step starts at 200–500 °C, with the conversion of cellulose, hemicellulose and lignin to oxygenated hydrocarbons called primary tar. Above 500 °C, primary tar is converted into phenolics and olefins compounds known as secondary tar. When the temperature is increased above 800 °C, part of the secondary tar converts to polycyclic aromatic compounds, also called tertiary [2].

Being mostly composed of hydrogen and carbon, tar is potentially a fuel. However, tar compounds can cause various problems such as condensation in cold spots, polymerization to form complex structures that condense even at high temperature, and formation of carbonaceous

\* Corresponding author. Leeghwaterstraat 39, 2628 CA, Delft, Netherlands.  
E-mail address: [a.cavalli@tudelft.nl](mailto:a.cavalli@tudelft.nl) (A. Cavalli).

<https://doi.org/10.1016/j.biombioe.2021.105982>

Received 27 September 2020; Received in revised form 6 January 2021; Accepted 24 January 2021

Available online 6 February 2021

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deposits which can deactivate catalysts or plug filter pores, gas lines and heat exchangers. The term carbonaceous deposit is used in this work to indicate a deposit mostly consisting of carbon, that might have originated from thermal cracking, catalytic reactions, or polymerization [3]. To avoid the aforementioned issues, tar is often removed from the gas stream at low or intermediate temperature (below 300 °C) via physical methods, or converted into useable gases at high temperature (above 1000 °C) via processes such as reforming.

Reforming consists in converting tar into CO and H<sub>2</sub> using CO<sub>2</sub> (dry reforming) or H<sub>2</sub>O (steam reforming). The process temperature can be lowered by using a catalyst, that can be added inside the gasifier (primary methods) or in a downstream reactor (secondary methods). Catalysts can be classified in several different ways and the most important distinction can be made between metal-based, or synthetic, catalyst (e. g., Ni and Fe based catalysts) and naturally-occurring, or mineral, catalysts (e.g., dolomite and olivine). Generally, mineral catalysts are less catalytically active, but also less expensive. The latter is a significant advantage since the use of catalyst increases the overall system cost [4]. Moreover, naturally occurring catalyst could exhibit higher tolerance to impurities, such as H<sub>2</sub>S and HCl, or simply be replaced in case of deactivation due to carbon deposition [5]. Therefore, despite the lower activity, mineral catalysts, such as dolomite and olivine, are thoroughly studied [6–9].

Most of the research on biosyngas tar reforming has focused on secondary and tertiary tar, since the majority of the gasifiers are operated in the temperature interval 700–1000 °C (downdraft and fluidized bed gasifiers) [10]. Selected representative compounds or real tar have been used in these studies. As an example, Ren et al. used toluene as model compound to study the effect on the reforming activity of different Ni loading methods and oxidation degree of the char support [11]. Recently, Ashok et al. reviewed the progress in the development of catalysts for steam reforming of biomass tar using toluene, benzene and naphthalene as tar model compounds [12]. Various catalysts have been compared by Simell et al. on the ability to reform tar generated in a full-scale updraft gasifier [13,14]. This research found that silicon carbide is an inert material and the activity of the catalysts decreases in the order Ni on Al<sub>2</sub>O<sub>3</sub> > dolomite > activated alumina > silica-alumina [14]. Other authors tested different materials, as Fuente-Cano et al., who studied the conversion of tar generated in a steam-blown fluidized-bed gasifier using wood char as catalyst [15]. Furthermore, innovative system configurations have been investigated by Savuto et al. who achieved tar reforming by placing metal-based catalysts inside the ceramic filter candles in the freeboard of a fluidized bed gasifier [16]. Nonetheless, updraft gasifiers present some advantages over downdraft and fluidized bed gasifiers: operability with a broad spectrum of feedstock (in terms of ash, moisture and size), very low particulate matter entrainment (both dust and ash), simplicity of construction, technology maturity and robustness and high efficiency [17]. On the other hand, updraft gasifiers have the disadvantage of producing a larger amount of tar, mostly belonging to the primary tar group.

Studies on biosyngas primary tar reforming are limited in literature. Most of primary tar have a molecular weight lower than that of benzene; therefore, they are often not considered as tar. Moreover, problems with tar such as condensation at high temperature and formation of carbonaceous deposits are promoted by aromatic hydrocarbons (secondary and tertiary tar). Conversely, primary tar are volatile compounds (e.g., formaldehyde, furan) or light condensable compounds (e.g., acetic acid, hydroxyacetone) with low condensation temperatures. Nonetheless, also primary tar represent a threat for downstream equipment due to their corrosiveness [18] and, if temperature is increased, their tendency to form carbonaceous deposits and harmful secondary/tertiary tar compounds via cracking or polymerization [19,20]. Furthermore, the wastewater generated by low temperature physical removal methods, such as scrubbing, has to be treated to prevent environmental issues caused by these organic molecules [21,22].

Some information on primary tar reforming can be derived from

studies on catalytic steam reforming of bio-oil and its representative compounds. In fact, bio-oil is a product of biomass pyrolysis and consists predominantly of a mixture of primary tar as aldehydes, alcohols and acids derived from the carbohydrate fraction of biomass, and phenolics derived from lignin [23]. Detailed reviews on catalytic reforming of bio-oil and its representative compounds can be found in literature [24–27]. In general, the activity of transition metal catalyst towards the steam reforming of acetic acid is Ni > Co > Fe > Cu [28]. Ni and Co are much more catalytically active than Fe and Cu, but less active than noble metals [29]. The majority of studies focus on metal-based catalyst, whereas a very limited amount of research has investigated natural catalysts, such as dolomite and olivine [30,31]. As with most tar compounds, one of the main reasons for catalyst deactivation in studies with bio-oil and its representative compounds is the formation of carbonaceous deposits. Studying the catalytic steam reforming of acetic acid on Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, An et al. concluded that the carbonaceous deposits originated from the catalytic cracking reactions and the CO disproportionation reaction [32]. With Pt/ZrO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts, the formation reaction of acetone via acetic acid condensation/dehydration was identified as the carbonaceous deposits formation mechanism [33]. Additionally, since the oxygenates are often thermally unstable, thermal cracking can also lead to carbonaceous deposits formation [34,35].

Although the studies on bio-oil and its representatives compounds (e. g., acetic acid) provide some insights, most studies use humidified N<sub>2</sub>, Ar or He as gas carrier [36–38]. However, the presence of CO, CO<sub>2</sub> and CH<sub>4</sub> in biosyngas can have a significant impact on the catalytic reforming of tar compounds [39]. In fact, CO<sub>2</sub> can increase tar conversion via dry reforming and gasify carbonaceous deposits, H<sub>2</sub> and CO can shift the reforming reaction equilibrium towards the reactants, and tar and biosyngas components might compete for catalysts active sites [40]. Therefore, this study evaluates the ability of three different catalysts to reform acetic acid, selected as main primary tar compound from updraft gasification, using simulated biosyngas as gas carrier. Particular attention was given to one of the catalysts tested, dolomite, owing to the promising results obtained and the opportunity this natural catalyst offers to decrease system costs. To the best of the authors knowledge, this represent one of the few, if not the first study focusing on acetic acid reforming under updraft gasification representative conditions. The insights presented are expected to help the further development of high temperature gas cleaning, and the commercialisation of energy conversion systems based on updraft biomass gasifiers.

## 2. Methodology

In this study, the ability of one metal-based catalyst and two mineral catalysts (i.e., dolomite and olivine) to reform acetic acid was compared using simulated biosyngas as gas carrier. The results are compared with a benchmark test performed using activated alumina. This material was selected since it is often used as support for metal-based catalyst and it shows limited catalytic activity. Biosyngas was used as gas carrier instead of a simple carrier (e.g., humidified N<sub>2</sub> and He) as it can have a significant impact on the reforming process. Moreover, the use of biosyngas gives the possibility to evaluate the catalyst activity towards methane reforming and Water-Gas-Shift (WGS) reactions, thus providing additional useful information for the design of tar reformers for updraft biomass gasifiers based systems.

Acetic acid was selected as model compound since it is the main component of primary tar, that is the largest group of tar generated in updraft gasifiers [2]. Above 500 °C primary tar undergoes the maturation process studied by Milne et al. [2]. Therefore, when the gas is heated up, some of the acetic acid might be converted into different compounds such as higher molecular weight compounds and carbonaceous particles even before reaching the catalyst bed, as observed also by Matas Güell et al. or by Boot-Handford et al. [33,41]. This conversion process is affected by the heating up conditions (e.g., surfaces available, residence time and temperature). Using acetic acid as initial compound

was considered a more interesting option as compared to using only a secondary tar compound, as it provides conditions representative of an updraft gasifier based system, where primary tar compounds, together with higher molecular weight compounds and carbonaceous particles generated when heating up the biosyngas containing primary tar compounds, reach the reformer. Therefore, in the experiments performed, the three catalysts are evaluated on the ability to convert residual acetic acid and higher molecular weight compounds, and to withstand the deposition of carbonaceous particles generated while heating up the gas mixture. All catalysts were tested under the same operating conditions and, in the case of dolomite, additional tests were performed: one at lower temperature (400 °C), and one at higher temperature (900 °C) and higher steam content (50.1 vol%). The low-temperature test was performed to investigate the influence of dolomite on the process of heating up biosyngas containing acetic acid. Other catalysts (i.e., Ni based catalysts) are in fact reported to promote the ketonization reaction already at 350 °C [42]. The high-temperature and high steam content test was performed to investigate the possibility to completely suppress accumulation of carbonaceous deposits. The results of these additional tests provide a useful direction for future research on using dolomite for reforming tar from biomass updraft gasifiers without the formation of carbonaceous deposits.

### 2.1. Operating conditions, setup and equipment

The tests were carried out in a bench-scale unit consisting of a quartz reactor mounted inside an electric furnace. The Process and Instrumentation Diagram (P&ID) of the unit is illustrated in Fig. 1. The electric furnace is an insulated ceramic hollow cylinder with a heating coil wrapped along its length. A thermocouple is placed at the middle of the cylinder height, on the inner cylinder surface, to control the temperature of the heating coil. The quartz reactor has an inner diameter of 2 cm and the catalyst bed, kept in place thanks to a quartz frit, has a height of 5.5 cm. A thermocouple is placed next to the top part of the catalyst bed to

monitor the temperature during the tests. Before starting the experimental campaign, this thermocouple was used to measure the temperature of the furnace along its length. The furnace showed a temperature gradient and, as a consequence, the catalyst bed was not kept at a uniform temperature: the bottom part was at 680 °C, while the top part at 750 °C. The top of the catalyst bed was placed at the highest temperature in the furnace. Fig. 2 shows the furnace and the design of the quartz reactor next to the temperature profile over the setup.

A gas flow rate of 380 NmL/min simulated biosyngas composed of 133.1 NmL/min H<sub>2</sub>, 8.9 NmL/min CO, 74.1 NmL/min CO<sub>2</sub>, 13.7 NmL/min CH<sub>4</sub>, 91.1 NmL/min H<sub>2</sub> and 59.1 NNmL/min N<sub>2</sub> (35.0 vol% H<sub>2</sub>O, 2.3 vol% CO, 19.5 vol% CO<sub>2</sub>, 3.6 vol% CH<sub>4</sub>, 24.0 vol% H<sub>2</sub> and 15.6 vol% N<sub>2</sub>) was used. The volume percentages correspond to the measured values during the first “FlexiFuel-SOFC” project experimental campaign. This EU funded project aimed at the development of a micro scale combined heat and power system composed of an updraft biomass gasifier, a high temperature gas cleaning unit and a solid oxide fuel cell (SOFC) [43,44]. The gas flow rates were regulated using mass flow controllers Bronkhorst EL-FLOW (Bronkhorst, The Netherlands). Steam was added to the fuel gas stream by bubbling the gas mixture (except CO<sub>2</sub>) in a temperature controlled water bath (humidifier). It was assumed that the gas in the water bath was constantly in equilibrium with the liquid phase. Therefore, the steam content is a function of the liquid temperature, according to Antoine’s equation. The piping after the humidifier and the bottom part of the quartz reactor were trace heated and kept at 150 °C.

The tar concentration at the inlet was 40 g/Nm<sup>3</sup>, and was selected based on the results of tar sampling from the “FlexiFuel-SOFC” project updraft gasifier that used wood chips as feedstock and humidified air as gasifying agent. The analysis was performed following the tar protocol (CEN TC BT/TF 143 WI CSC 03002.4) [1]. Liquid acetic acid of 99.7% purity (Sigma Aldrich, USA) was injected at the entrance of the quartz reactor using a peristaltic pump BT100-2 J (Longer Precision Pump Co., China). The trace heating temperature assured the continuous evaporation of the acetic acid. With the steam and acetic acid flow rates selected, the steam-to-carbon (S/C) ratio results equal to 1.3 and to 1.8 for the tests performed with dolomite at 900 °C and different gas composition.

At the reactor outlet, a three way valve directed the gas flow either to a series of impinger bottles for tar sampling, or to a microGC to monitor the outlet gas composition. An Agilent 490 microGC with thermal conductivity detector and a CP-COX column for measuring CO, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> (Agilent, USA) was used. Before reaching the microGC, the gas was passed through a condenser and a desiccator containing silica-gel to remove the moisture contained in the gas. The outlet flow rate was back-calculated from the inlet N<sub>2</sub> flow rate and the N<sub>2</sub> outlet concentration that was measured with the microGC. This was then used to calculate the flow rates of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>. The outlet tar concentration was measured by bubbling the outlet gas flow in a series of 4 impinger bottles, the first one kept empty and acting as moisture collector, two containing isopropanol at room temperature, and a last one containing isopropanol at 0 °C. The isopropanol and water samples were analyzed with a Varian 430 GC-FID (Agilent, USA) equipped with a Rtx-1 column (Restek, USA).

The catalyst used were all in the form of particles with a diameter of 2–3 mm. The metal-based catalyst was a commercially available catalyst called TARGET™ developed specifically for tar reforming by the company Nexceris and consisted of Pt/MNS (MgO, NiO, SiO<sub>2</sub>). The olivine used is produced by the manufacturer specifically for biomass gasifiers bed, and the material is reported to have a catalytic activity close to that of calcined dolomite [45]. The dolomite was supplied in partially calcined form (CaCO<sub>3</sub>·MgO), that is with MgCO<sub>3</sub> already converted into MgO and with Ca still in the form of CaCO<sub>3</sub>. An additional calcination process was performed at 900 °C to increase the dolomite catalytic activity. However, the catalyst became too brittle; consequently, the calcination temperature was lowered to 800 °C but the dolomite

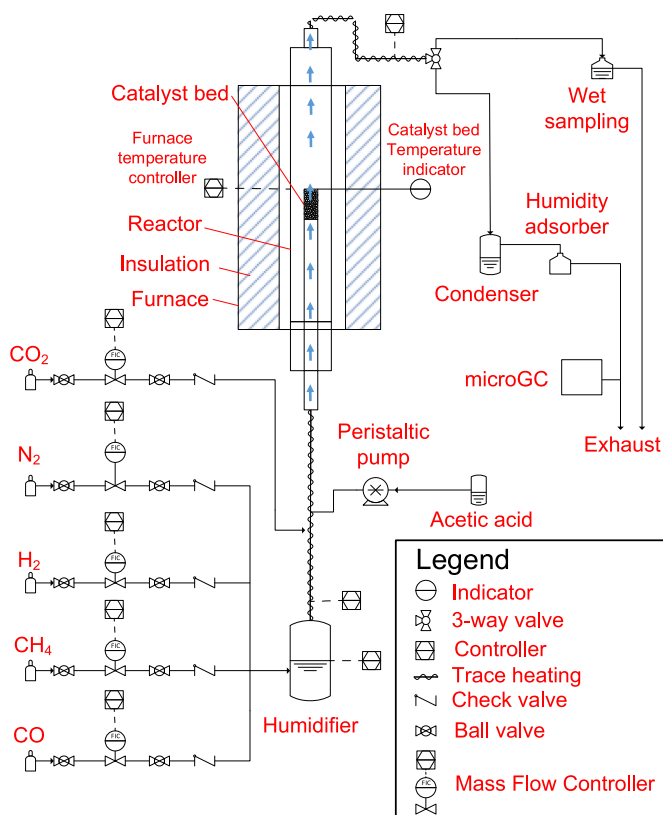


Fig. 1. P&ID of the test station.

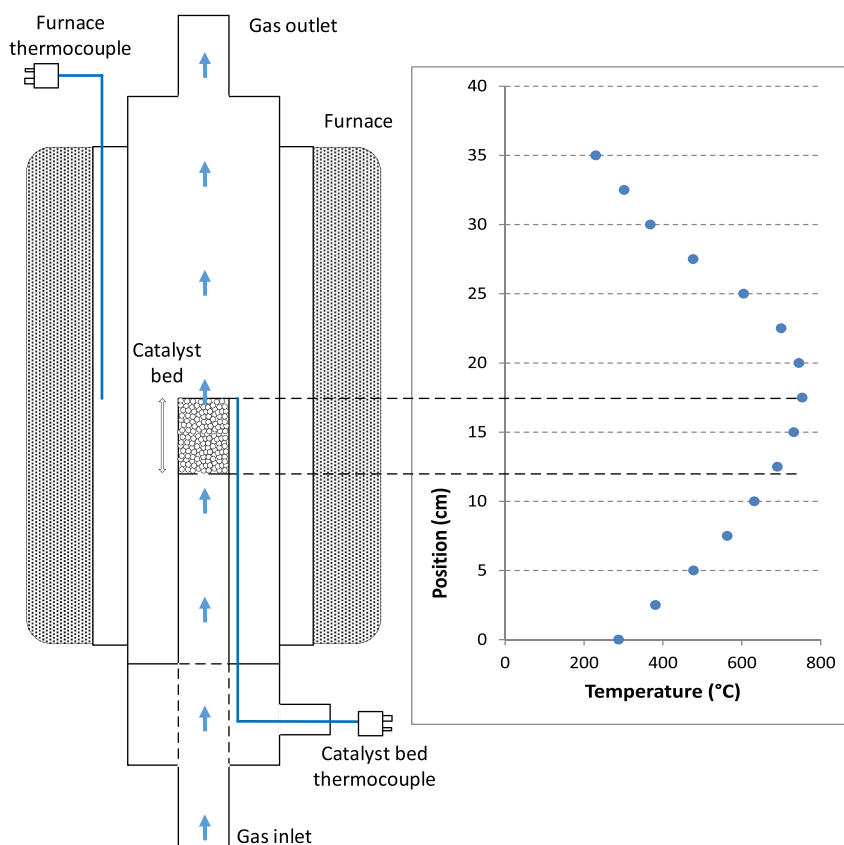


Fig. 2. Simplified representation of the quartz reactor and temperature profile over the furnace and the catalyst bed.

mechanical resistance was still significantly affected. Therefore, the dolomite used in the tests was in the partially calcined form as received from the supplier. The chemical composition of the partially-calcined dolomite and of the olivine is shown in Table 1.

## 2.2. Testing procedure

After having positioned the quartz reactor in the furnace, the temperature was increased to the set value with a ramp of 50 °C/h. A nitrogen flow of 100 NmL/min was passed through the catalyst bed during the heating up stage. The gas flow rate was then changed to simulated biosyngas and the gas composition was monitored for 12 h before adding acetic acid. In the case of the metal-based catalyst, acetic acid was injected after 18 h. The longer time was used to assure full reduction of the catalyst. The gas composition at the outlet of the reactor was monitored during this time to determine the catalyst activity towards WGS and methane reforming and to be sure that the catalyst was not undergoing any change affecting its catalytic activity.

Acetic acid was successively injected and the experiment was kept running for three days. During the day the outlet gas composition was

monitored with the microGC while during the night the outlet gas was led through the sampling bottles to measure the residual tar content with the GC. The gas composition results presented are the average values recorded over time. After the three days operation, the setup was cooled down with a ramp rate of 50 °C/h and a gas flow rate of 100 NmL/min N<sub>2</sub> passing through the catalyst bed. The catalyst was then visually inspected for carbonaceous deposits. An elemental and morphological analysis of the deposit was not performed since the scope of this work was limited to the performance comparison of the different catalysts, and to the identification of a suitable material and conditions to be used in an integrated biomass gasifier SOFC microCHP system. Table 2 summarises the tests performed and the relevant parameters.

## 2.3. Thermodynamic equilibrium calculations

Before proceeding with the experimental tests, thermodynamic equilibrium calculations were performed using the software FactSage version 5.4.1 (Thermfact/CRCT, Montreal, Canada and GTT-Technologies, Aachen, Germany) to assure the catalysts were operated outside the theoretical solid carbon formation region [46]. The results of the calculations also provide an indication of the expected gas composition at the outlet of the catalyst bed if thermodynamic equilibrium conditions are reached. The software calculates the concentrations of chemical species when specified elements or compounds react to reach a state of chemical equilibrium. The users specifies the mass of the reactants, process temperature and pressure, and the software solves a Gibbs minimization algorithm based on three constraints: the equilibrium product amounts are positive, the mass balance with respect to the system components is satisfied and correspond to the lowest possible Gibbs energy for the possible products. A detailed explanation on the method followed for the calculation can be found on the specific software webpage [47]. Thermodynamic equilibrium calculations only give an indication of the possibility for solid carbon formation since

Table 1

Chemical composition in mass percentage of the partially calcined dolomite and of the olivine received from suppliers.

	Partially-calcined dolomite [wt%]	Olivine [wt%]
CaCO <sub>3</sub>	68.9	
CaO	1.4	max 0.4
MgO	25.4	47.5–50.0
MgCO <sub>3</sub>	0.5	
Fe <sub>2</sub> O <sub>3</sub>	0.5	8.0–10.5
Al <sub>2</sub> O <sub>3</sub>	0.2	
SiO <sub>2</sub>	0.4	39.0–42.0
H <sub>2</sub> O	2.7	

**Table 2**  
Synoptic table summarising the tests performed and the relevant parameters.

Catalyst	Bead Size (mm)	Gas Composition (NmL/min)	Gas Composition (vol%)	Gas flow Rate (NmL/min)	Inlet tar Concentration (g/Nm <sup>3</sup> )	Catalyst bed Temperature bottom – top (°C)	Test Duration (h)
Alumina	2–3	133.1 H <sub>2</sub> O,	35.0 H <sub>2</sub> O,	380	40	680–750	72
Olivine		8.9 CO,	2.3 CO,				
Metal-based		74.1 CO <sub>2</sub> ,	19.5 CO <sub>2</sub> ,				
Dolomite 1		13.7 CH <sub>4</sub> ,	3.6 CH <sub>4</sub> ,				
Dolomite 2		91.1 H <sub>2</sub> ,	24.0 H <sub>2</sub> ,			T <sub>top</sub> = 400	
		59.1 N <sub>2</sub>	15.6 N <sub>2</sub>				
Dolomite 3		190.2 H <sub>2</sub> O,	50.1 H <sub>2</sub> O,			T <sub>top</sub> = 900	
		60.3 CO,	15.9 CO,				
		22.7 CO <sub>2</sub> ,	6.0 CO <sub>2</sub> ,				
		13.7 CH <sub>4</sub> ,	3.6 CH <sub>4</sub> ,				
		33.0 H <sub>2</sub> ,	8.7 H <sub>2</sub> ,				
		60.1 N <sub>2</sub>	15.8 N <sub>2</sub>				

equilibrium might not be reached during the test. Moreover, the software database used contains only thermodynamic properties of solid carbon in the form of graphite.

### 3. Results

Fig. 3 shows the carbon-hydrogen-oxygen ternary diagram calculated using the software FactSage. A specific mixture containing these elements is represented by a point in the diagram. The operating points without tar (triangle) and with tar (dot) were calculated taking into account all the biosyngas compounds containing hydrogen, oxygen and carbon. In the diagram, two regions can be distinguished, one where solid carbon is formed and one where the mixture completely remains in the gas phase. The two regions are delimited by a line whose position depends on the temperature. If the operating point falls on the left of the line, then solid carbon is formed at equilibrium. The results indicate that, if equilibrium conditions are reached, no carbonaceous deposits should be present in the whole temperature interval in which the catalyst was operated. Both operating points in fact fall on the right of the continuous and of the dotted line, representing the operating temperatures of 750 °C and 680 °C, respectively.

The software was also used to calculate the equilibrium gas composition of clean biosyngas at 750 °C with and without acetic acid,

as illustrated in Table 3. If equilibrium is reached, methane is almost completely reformed and an increase in the carbon monoxide flow rate is expected because of the reverse water gas shift (RWGS) reaction occurring in the reactor. Despite hydrogen is converted into water by the RWGS reaction, the outlet flow rate is higher than the inlet flow rate due to methane being reformed. Similarly, the flow rate of water remains almost constant since the amount produced via the RWGS is balanced by the amount consumed via methane reforming. When acetic acid is added to biosyngas, its conversion leads to an increase in H<sub>2</sub> and CO, and to a minor extent of CO<sub>2</sub> flow rates.

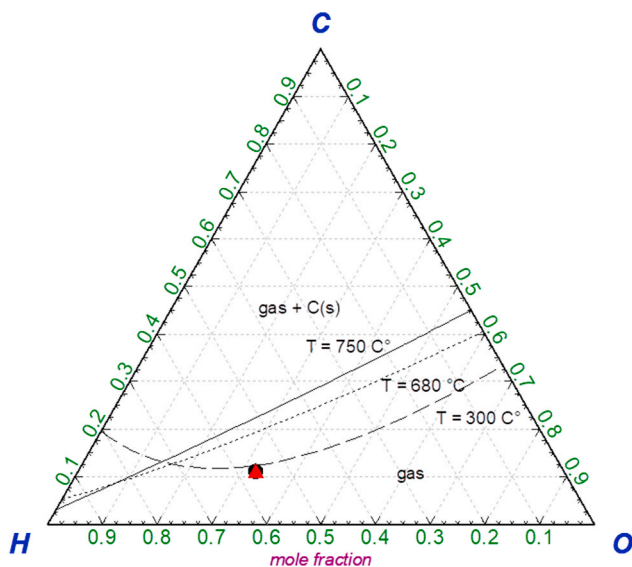
A pre-test was performed without filling the reactor with any catalyst to determine whether reactions towards equilibrium take place at 750 °C even without any catalyst. The gas composition measured at the outlet of the furnace, shown in Fig. 4, indicates that the residence time was not sufficient to allow any reaction to a noticeable extent. The minor differences between the set and measured inlet values were probably caused by small inaccuracies in the mass flow controllers' calibration. During this test, the inlet concentration of acetic acid was also measured by wet sampling and the results show an inlet concentration of 37–41 g/Nm<sup>3</sup>, corresponding to a gas volume flowrate of 3.4–3.8 NmL/min.

#### 3.1. Reference test – alumina

The reference test with activated alumina beads in the reactor showed that alumina interacts with the gaseous species but it is not significantly catalytically active. Fig. 5 shows the gas composition at the inlet and at the outlet of the reactor when biosyngas with and without acetic acid was passing through the alumina bed. While the flow rate of CH<sub>4</sub> remained unchanged, H<sub>2</sub> and CO<sub>2</sub> reacted and formed CO via the reverse water gas shift reaction. When acetic acid was added to the biosyngas, there was an increase in the methane outlet flowrate, while the other compounds remained almost unchanged. This shows that part of the acetic acid undergoes cracking to CH<sub>4</sub> rather than catalytic reforming leading to CO, H<sub>2</sub> and CO<sub>2</sub>, as observed by Basagiannis et al. [42]. Unfortunately, the microGC was not calibrated for any hydrocarbon other than methane nor for oxygen. Moreover, the water condensed

**Table 3**  
Inlet and equilibrium outlet gas flow rates at 750 °C.

	Inlet set (NmL/min)	Outlet equilibrium clean biosyngas (NmL/min)	Outlet equilibrium biosyngas + acetic acid (NmL/min)
H <sub>2</sub> O	133.1	135.0	132.5
H <sub>2</sub>	91.1	116.4	128.1
CO <sub>2</sub>	74.1	58.5	61.2
CO	8.9	38.1	44.7
CH <sub>4</sub>	13.7	0.1	0.1
CH <sub>3</sub> COOH	4.6	/	0.0



**Fig. 3.** C–H–O ternary diagram indicating the carbon formation region at 680 °C and 750 °C and the operating point with clean biosyngas (triangle) and with acetic acid (dot).

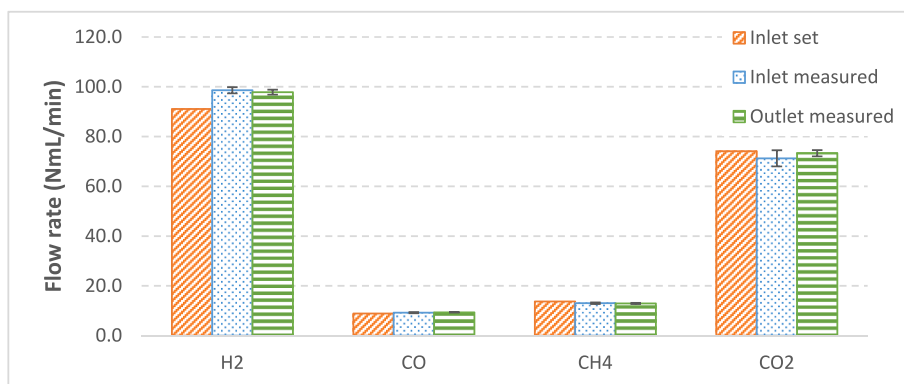


Fig. 4. Measured inlet and outlet gas composition without catalyst in the reactor kept at 750 °C.

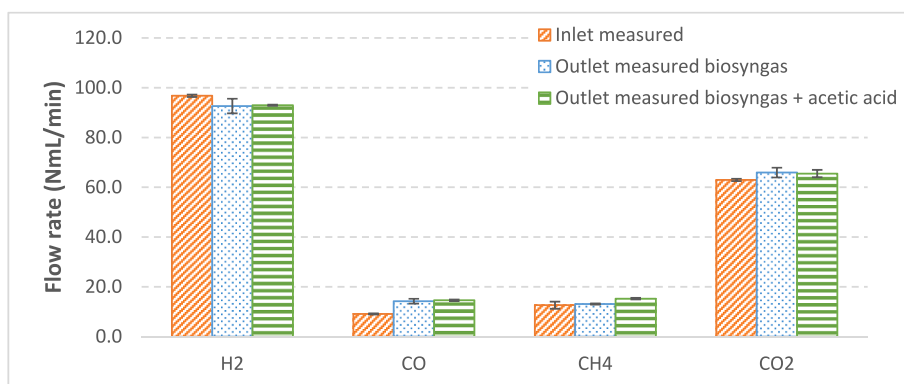


Fig. 5. Measured gas composition with alumina beads in the reactor.

at the outlet of the reactor and the amount and composition of the carbonaceous deposits were not measured. It is therefore not possible to give details on the acetic acid thermal decomposition pathway. The study of acetic acid decomposition mechanism is however considered beyond the scope of this paper.

No acetic acid was detected at the reactor outlet by wet sampling. However, an amount of hydroxyacetone between 0.07 and 0.45 g/Nm<sup>3</sup> was measured. In this test, the first bottle of the sampling train was filled with 30 ml of isopropanol. The mix of isopropanol and condensed water contained in the first bottle turned slightly yellow and had a distinct odour typical of aromatic compounds. This might indicate that part of the acetic acid underwent the maturation process described in Ref. [2]. Nonetheless, the analysis with GC-FID did not show any tar compound. This could have been due to the inability of the column to separate the compounds, or to the high dilution caused by the water condensed in the first sampling bottle. Gravimetric analysis could have been performed on the liquid samples to confirm the presence and quantify the total amount of compounds that were not being detected by GC-FID analysis. To avoid dilution in the successive tests, the first bottle was kept empty and served as moisture collector.

At the end of the test, the alumina beads were fully covered with carbonaceous deposits. In literature it is reported that acidic supports as Al<sub>2</sub>O<sub>3</sub> have the tendency to cause a larger amount of carbonaceous deposits as opposed to basic supports which enhance water adsorption [29, 42]. The deposit was also present on the reactor walls where the temperature was above 400 °C, that is even before the catalyst bed. Therefore, the carbonaceous deposits might have formed directly in the bed, and/or it might have formed during the heating up process, after which the carbonaceous particles accumulated in the bed by a filtering effect. The formation of carbonaceous deposits on the reactor walls might have occurred due to a radial temperature gradient resulting in higher temperature near the surface, or to acetic acid reacting on the

reactor surface. From the experiment performed it is not possible to know if the conversion of acetic acid was complete even before reaching the alumina bed. To better understand the thermal cracking of acetic acid and causes for carbon deposits on the reactor wall and catalytic bed, a test with an empty reactor could be performed. Nonetheless, the understanding of acetic acid thermal cracking behaviour was considered outside the scope of this study and the results of the tests with alumina represent the base case for the comparison of the three catalysts tested.

### 3.2. Olivine catalyst

Fig. 6 presents the gas composition when olivine was used as catalyst. The catalyst showed a very limited catalytic activity towards the reverse water gas shift reaction and did not significantly catalyse methane reforming. Moreover, when acetic acid was added to biosyngas, there was an increase in the methane outlet flowrate. However, also the flow rates of CO, H<sub>2</sub> and CO<sub>2</sub> slightly increased which might indicate the occurrence of acetic acid catalytic reforming.

The wet sampling showed no acetic acid at the reactor outlet and no other compound was detected during the first two days of measurement. Nonetheless, the third day of sampling 0.02–0.19 g/Nm<sup>3</sup> of hydroxyacetone were measured, which might indicate that the catalytic activity was reducing over time. For this reason, the test was extended for an extra day and during the next sampling the amount of hydroxyacetone increased to 0.14–0.30 g/Nm<sup>3</sup>, thus confirming a decreased activity of the catalyst.

After having cooled down the furnace, carbonaceous deposits considerably covered the catalyst bed. The acetic acid was therefore completely converted into non-condensable gases and carbonaceous deposits, at least during the first two days of operation. Also in this case, the deposits were found also on the reactor walls. It is not known if the carbonaceous deposits on the catalyst originated from reactions in the

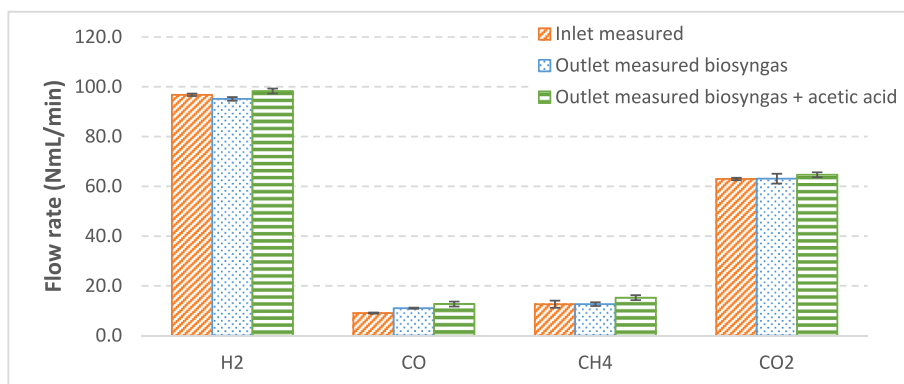


Fig. 6. Measured gas composition with olivine in the reactor.

catalytic bed and/or might have formed before the catalyst, carried by the gas and then filtered by the catalyst bed.

### 3.3. Dolomite catalyst

The results in Fig. 7 show that roughly 10 NmL/min of H<sub>2</sub> reacted with CO<sub>2</sub> to form CO, thus indicating that dolomite is catalytically active for the reverse water gas shift reaction. The outlet CO flow rate is still far from the value expected at equilibrium, partially due to the lack of catalytic activity of dolomite towards methane reforming, and partially to the reverse water gas shift reaction not reaching equilibrium. When acetic acid was added to the biosyngas, methane outlet flow rate increased while the flow rates of the other compounds remained almost unchanged.

Tar sampling indicated that all acetic acid was converted, and no other compounds were found at the reactor outlet. At the end of the test, carbonaceous deposits were present on the reactor walls and on the catalyst. Therefore, acetic acid was converted into non-condensable gases and carbonaceous deposits. Interestingly, the deposits were found only in the first 2.5 cm of the catalyst bed, while the top part was clean. This might have been due to the conversion of all acetic acid and intermediates taking place before this top section or to the ability of the catalyst to convert acetic acid without carbonaceous deposits formation. Another explanation might be that from 2.5 cm onwards, the bed temperature was sufficiently high to allow the gasification of the carbonaceous deposits filtered. However, it seems unlikely that the carbonaceous deposits accumulated on the catalyst by filtration were oxidized again under the testing conditions, that is a reducing atmosphere and moderate temperatures. Therefore, it is more likely that the catalyst was active towards acetic acid conversion without carbonaceous deposits formation. Fig. 8 shows a schematic of the process described.

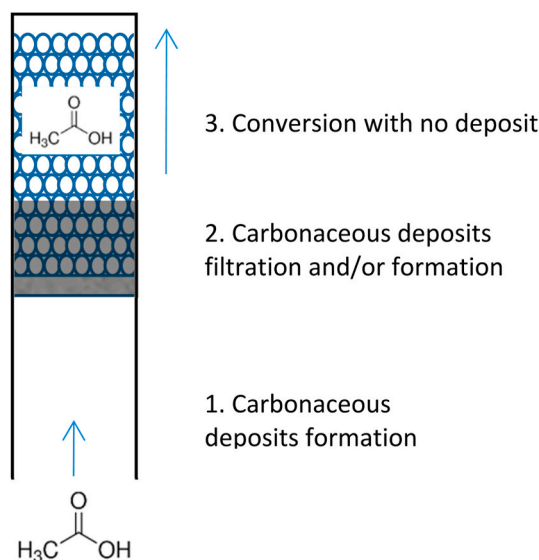


Fig. 8. Carbonaceous deposits formation and deposition along dolomite catalyst bed.

An additional test was performed keeping the top of the catalyst bed at 400 °C to investigate the influence of dolomite on the process of heating up biosyngas containing acetic acid. Moreover, considering that dolomite appeared not to suffer any deposition at temperatures above roughly 730 °C, an additional test was performed to verify the possibility to suppress carbonaceous deposits accumulation completely. In this second test, a different gas composition was used, with a water flow rate of 190 NmL/min, corresponding to 50% vol, and the top of the bed kept

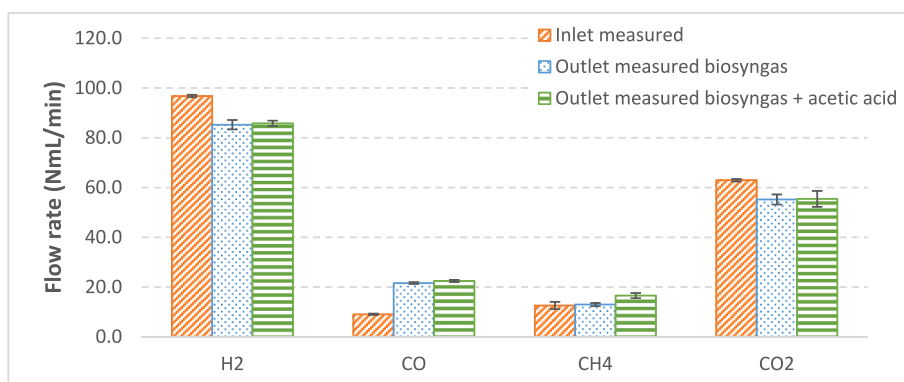


Fig. 7. Measured gas composition with dolomite in the reactor.

at 900 °C. Fig. 9 compares the measured flow rates with the calculated equilibrium flow rates. At both the temperatures tested, the gas composition was far from equilibrium. At low temperature, that is 400 °C, while CO should be absent and the H<sub>2</sub> content is supposed to be significantly lower than the measured values, the CH<sub>4</sub> flow rate should be higher than the inlet value due to methane formation reaction. However, dolomite is not catalytically active towards methane formation or reforming reactions, as visible also from the outlet methane flowrate measured at 900 °C, that is almost equal to the inlet value and higher than the expected equilibrium amount.

Fig. 10 and Fig. 11 show the gas composition measured at the inlet and outlet of the reactor in the two tests. The test at low temperature clearly showed that dolomite had no catalytic activity at this temperature. This was confirmed by the sampling at the outlet which resulted in an amount of acetic acid equal to 35.5–39.4 g/Nm<sup>3</sup>, corresponding to 3.3–3.6 NmL/min. At the end of the test, the dolomite at the top of the bed was light grey, indicating a very minor presence of carbonaceous deposits. At this temperature also thermal cracking of acetic acid almost did not take place, in accordance with the observations of An et al. [32]. In the test at high temperature, that is 900 °C, the water gas shift reaction occurred while the methane content remained almost unchanged. Interestingly, a slightly more evident increase in H<sub>2</sub> and CO flow rates was noticed as compared to the tests at lower temperatures, suggesting the occurring of acetic acid catalytic reforming. No acetic acid or other tar compound was measured at the reactor outlet and no carbonaceous deposits were observed.

The results obtained might have been due to the higher temperature or the higher steam content in the gas since both variables are expected to suppress the formation of carbonaceous deposits. The results therefore provide only a preliminary indication of the possibility to suppress carbonaceous deposits accumulation. However, as experienced during the pre-calcination tests at 800 °C and 900 °C, the catalyst became excessively brittle, with some of the catalyst beads at the top of the bed losing their structure. The loss of mechanical strength of dolomite might be explained by the occurrence of secondary calcination, converting the partially-calcined dolomite (MgO–CaCO<sub>3</sub>) to full-calcined dolomite (MgO–CaO). Half-calcined dolomite is a rigid and strong material whereas full-calcined dolomite can be very fragile [48]. The secondary calcination reaction depends on process temperature and CO<sub>2</sub> partial pressure; upon checking the secondary calcination temperature with thermodynamic equilibrium calculations, it can be noticed that secondary calcination is expected to occur approximately at 750–760 °C. Therefore, further tests maintaining the dolomite temperature below 750 °C and with high amounts of steam are suggested to identify under which circumstances carbonaceous deposit accumulation can be suppressed without compromising the catalyst attrition resistance.

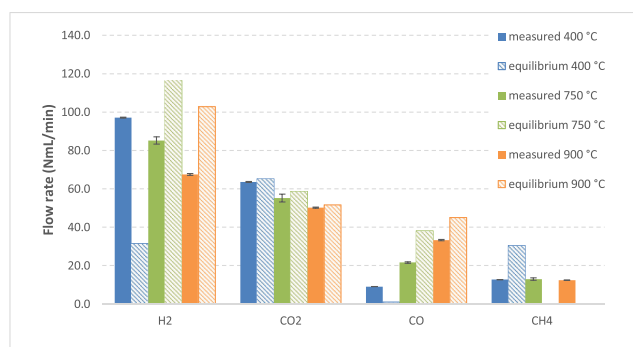


Fig. 9. Comparison between outlet measured (fill) and equilibrium (pattern) flow rates at the temperatures tested without acetic acid in the biosyngas.

### 3.4. Metal-based catalyst

The biosyngas composition changed significantly when passing through the metal-based catalyst bed. The outlet flow rates of CO<sub>2</sub> decreased while that of CO increased due to the reverse water gas shift reaction. The H<sub>2</sub> outlet flow rate increased due to almost complete reforming of CH<sub>4</sub>. The gas composition is very close to the expected equilibrium composition presented in Table 3, for both clean biosyngas and acetic acid containing biosyngas. The increase in H<sub>2</sub> and CO flow rates when acetic acid was injected indicates the occurring of reforming of acetic acid but also the reforming of the CH<sub>4</sub> generated during acetic acid thermal decomposition during the heating up process. Fig. 12 presents the gas composition measured at the outlet of the reactor with and without acetic acid.

Wet sampling showed no traces of any tar compounds, thus indicating the complete conversion of acetic acid into non-condensable gases and a very minor amount of carbonaceous deposits. Carbonaceous deposits were found on the reactor walls before the bed, and only a very minor amount was found on the first 0.5 cm of the catalyst bed; this deposit might have been filtered or formed in this section of the bed. Irrespectively from the formation mechanism, it can be concluded that at this temperature the metal based catalyst was able to almost completely suppress the accumulation of carbonaceous deposits.

### 3.5. Catalysts comparison and discussion

Table 4 summarises the results previously discussed to facilitate a comparison between the different catalysts.

Fig. 13 compares the gas composition measured at the reactor outlet with the different catalysts tested when biosyngas containing acetic acid was passed through the bed. It can be seen that in terms of catalytic activity towards the reverse water gas shift reaction and methane reforming, the metal-based catalyst has the best performances, with the outlet gas composition being almost equal to the expected equilibrium composition. Both dolomite and olivine showed some catalytic activity towards the reverse water gas shift reaction, with dolomite being more active than olivine. Neither dolomite nor olivine showed activity towards methane reforming and only some activity towards acetic acid reforming, with the majority of the primary tar being converted into methane and carbonaceous deposits. The result are in good agreement with literature, where it is often stated that metal-based catalysts outperform naturally-occurring catalysts [14].

The metal-based catalyst also appeared as the most capable of suppressing carbonaceous deposits accumulation. The catalysts can be sorted as olivine > dolomite > metal-based from the highest to the lowest amount of deposits accumulated during the test. From the experiment performed, it is not possible to know if the carbonaceous deposits found on the catalysts were formed in the bed or before it. However, irrespectively from the formation mechanism, it is clear that olivine similarly to alumina was not able to suppress carbonaceous deposits accumulation, while dolomite above roughly 730 °C and the metal-based catalyst already around 680 °C did not suffer carbonaceous deposits accumulation. Moreover, while dolomite and metal-based catalyst completely converted acetic acid into non-condensable gases for the whole duration of the test, the performances of olivine appeared to decrease in time and, at the end of the third and the additional fourth testing day, small amounts of hydroxyacetone were found. Hydroxyacetone is a common intermediate product in the conversion of carboxylic acids, such as acetic acid, into ketones via ketonization reaction [35,49].

The olivine used in this study is reported to have a catalytic activity close to that of calcined dolomite [45]. However, according to the manufacturer information, the material was sintered in a rotary kiln at 1600 °C for 3 h and, according to Corella et al. the sintering process strongly decreases the catalyst pore structure [50]. This might explain the performance of olivine observed in this study. Moreover, also Quan

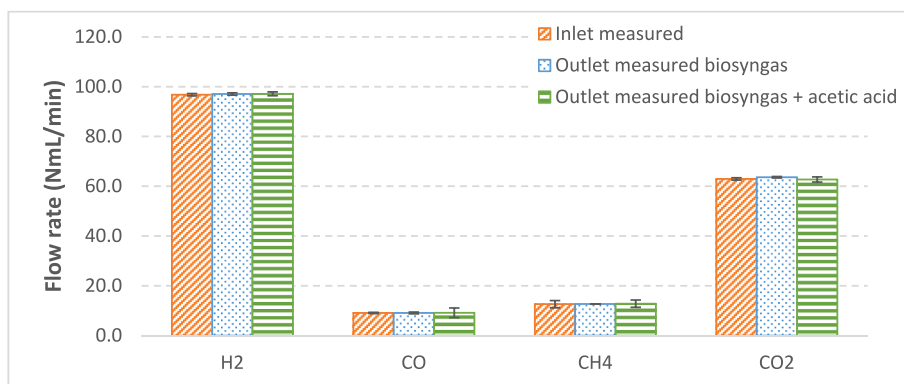


Fig. 10. Measured gas composition with dolomite in the reactor at 400 °C.

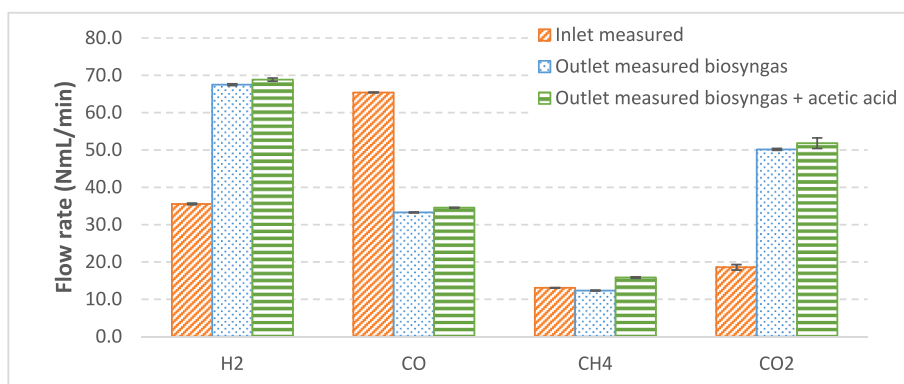


Fig. 11. Measured gas composition with dolomite in the reactor at 900 °C.

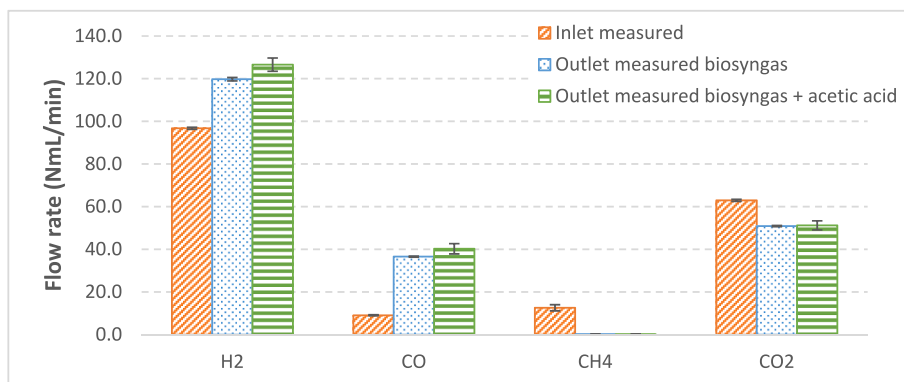


Fig. 12. Measured gas composition with metal-based catalyst in the reactor.

et al. observed a decrease in the catalyst performance of olivine due to calcination at higher temperatures [31]. However, since there are studies indicating that calcination might improve the performance of raw olivine [51], further investigation of the performances of raw and calcined olivine are suggested as future work. In case of dolomite, the catalyst used had a low iron content and literature indicates the iron promotes catalytic tar reforming and the WGS reaction [52]. Most importantly, dolomite was used in partially calcined form with Mg being in oxide form but Ca in the carbonate form. An additional test was attempted using dolomite that was pre-calcined at 800 °C. However, the gas flow rate was shortly stopped due to dolomite becoming powder and clogging the reactor. Moreover, the biosyngas atmosphere in our tests contained a high concentration of CO<sub>2</sub> and upon checking with equilibrium calculations, it is possible that CO<sub>2</sub> reacted with CaO and formed

CaCO<sub>3</sub> at temperatures lower than 800 °C. This form of Ca is believed not to be significantly catalytically active [53]. Nonetheless, the tests in this study showed that dolomite can almost completely convert the acetic acid and intermediate compounds into non-condensable gases at 680–750 °C, with the carbonaceous deposits present only in the bottom part of the bed. Dolomite friability and release of fines might limit its use as tar reforming catalyst. However, this issue could be mitigated by adding a particle filtration system downstream the catalytic bed. Alternatively, more resistant catalysts should be developed, as studied by Miao et al. who prepared catalysts based on dolomite, clay and carboxyl methyl cellulose with increased strength resistance and higher porosity [30].

The metal-based catalyst appeared to outperform the naturally-occurring catalysts with regard to reforming and resistance to

**Table 4**  
Summary of the results obtained.

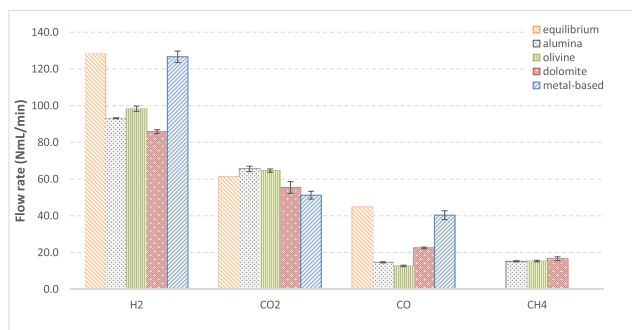
Catalyst	Outlet tar concentration (g/Nm <sup>3</sup> )	Outlet gas Composition (NmL/min)	Calculated equilibrium outlet gas composition (NmL/min)	Additional observations
Alumina	0.07–0.45 g/Nm <sup>3</sup> hydroxyacetone	H <sub>2</sub> 93.1 CO <sub>2</sub> 65.5 CO 14.6 CH <sub>4</sub> 15.2	H <sub>2</sub> 128.1 CO <sub>2</sub> 61.2 CO 44.7 CH <sub>4</sub> 0.1	No CH <sub>4</sub> reforming; No AA reforming; No RWGS reaction; slightly yellow condensed water with odour typical of aromatic compounds; beads fully covered by carbonaceous deposits.
Olivine	0.02–0.19 g/Nm <sup>3</sup> hydroxyacetone on III day and 0.14–0.30 g/Nm <sup>3</sup> on IV day	H <sub>2</sub> 98.3 CO <sub>2</sub> 64.6 CO 12.7 CH <sub>4</sub> 15.3		No CH <sub>4</sub> reforming; Minor AA reforming; Active towards RWGS reaction; Catalyst considerably covered by carbonaceous deposits
Metal-based	No tar at outlet	H <sub>2</sub> 126.6 CO <sub>2</sub> 51.2 CO 40.3 CH <sub>4</sub> 0.1		Complete CH <sub>4</sub> and AA reforming; Active towards RWGS reaction; Very minor amount of carbonaceous deposits on the low temperature part of the bed
Dolomite	No tar at outlet	H <sub>2</sub> 85.8 CO <sub>2</sub> 55.4 CO 22.5 CH <sub>4</sub> 16.6		No CH <sub>4</sub> reforming; Minor AA reforming; Active towards RWGS reaction; Carbonaceous deposits only on first part of the bed
Dolomite 2 T <sub>max</sub> = 400	35.5–39.4 g/Nm <sup>3</sup> acetic acid	H <sub>2</sub> 97.1 CO <sub>2</sub> 62.7 CO 9.2 CH <sub>4</sub> 12.8	H <sub>2</sub> 31.6 CO <sub>2</sub> 65.1 CO 38.1 CH <sub>4</sub> 30.5	No CH <sub>4</sub> reforming; Minor AA reforming; Active towards RWGS reaction; very minor amount of carbonaceous deposit at the top of the bed
Dolomite 3 T <sub>max</sub> = 900	No tar at outlet	H <sub>2</sub> 68.9 CO <sub>2</sub> 51.2 CO 34.6 CH <sub>4</sub> 15.8	H <sub>2</sub> 102.8 CO <sub>2</sub> 51.6 CO 45.1 CH <sub>4</sub> /	No CH <sub>4</sub> reforming; No AA reforming; No RWGS reaction; No carbonaceous deposit but beads very brittle

carbonaceous deposits accumulation. However, it might suffer poisoning from other contaminants usually present in biosyngas, as chlorine and sulfur, and it has the disadvantage of higher cost [4]. Moreover, the lack of catalytic activity of olivine and dolomite towards methane reforming is not necessarily a drawback. This compound can remain in biosyngas and be used directly in downstream processes without causing issues in some applications for heat and electricity production. With some conversion technologies, such as solid oxide fuel cells, the presence of methane in biosyngas even increases the system efficiency owing to the cooling effect of direct internal methane reforming [54].

Despite the differences in the operating conditions (temperature, space velocity, gas composition, tar concentration, and steam-to-carbon ratio), the tar abatement efficiency of the catalysts tested in this study can be compared with results found in literature. A short overview is illustrated in Table 5, where the catalyst tested and the abatement efficiencies are summarized. The most effective catalyst reported in literature are noble (i.e. Rh-, Pd-, Pt-) and transition (predominantly nickel) metal-based catalyst, followed by calcined dolomite, olivine, biochar, and ash. Ferrous metal oxides, clay, activated alumina, and

fluid cracking catalyst are generally less effective. Several studies comparing catalyst with tertiary tar indicate a similar order of the catalyst based on their activity [55,56]. The high tar abatement efficiency of the commercial nickel catalyst (100%) found in this work agrees well with figures commonly found in literature on acetic acid reforming with Ni/Al<sub>2</sub>O<sub>3</sub> [28,42,56–58] and several noble metal-based catalyst [59,60]. Furthermore, in this study the complete conversion of acetic acid was observed with dolomite and such abatement efficiencies have been previously reported [30,37]. The olivine in this work initially achieves a complete conversion of acetic acid as reported by Kechagiopoulos et al. [61,62]; however, with time the formation of carbonaceous deposits seemed to reduce the catalytic activity. The alumina catalyst studied in this work displayed a lower catalytic activity than the nickel, dolomite and olivine, which agrees with the lower tar abatement efficiencies of alumina supports reported in literature [29, 63]. Although most catalyst in Table 5 obtain lower efficiencies than transition/noble metal based catalyst, these compounds are often used as support materials.

The formation of carbonaceous deposits on the catalyst and sulfide poisoning can severely limit the tar abatement efficiency and lifetime of catalyst. Therefore, regeneration techniques such as air oxidation and application H<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> at elevated temperature are developed to remove carbonaceous deposits on spent catalyst and recover the activity of the catalyst [76]. For example, after oxidizing the carbonaceous deposit on nickel catalyst at 750 °C catalytic activity could be completely regained [77]. Regeneration techniques are also very promising for less active catalyst or catalyst more prone to deactivation by carbonaceous deposits as it allows using less expensive catalyst for tar removal [78]. Lind et al. applied air to a catalyst regeneration unit located next to the tar reformer and continuously replaced older catalyst, namely ilmenite (FeTiO<sub>3</sub>) with regenerated catalyst, thereby continuously removing carbonaceous deposits and maintaining a tar conversion of 35% [78]. Although catalyst regeneration is promising, the cyclic high temperature processing can for example lead to nickel sintering, phase transformations and volatilization [79] and recent studies show that regeneration is still an important topic of research [76].



**Fig. 13.** Comparison of outlet gas composition measured with the different catalysts tested.

**Table 5**  
Overview of previous studies on acetic acid and bio-oil reforming using different catalysts.

Catalyst	Model compound	Tar abatement efficiency	Reference
Natural rocks			
Calcined dolomite	Primary tar mixture/bio-oil	99–100%	[37]
	Acetic acid	99.7%	[30]
	Primary tar mixture/bio-oil	40%	[64]
	Primary tar mixture/bio-oil	40–80%	[52]
Olivine	Acetic acid	15%	[65]
	Acetic acid	100%	[61]
	Primary tar mixture/bio-oil	75–100%	[62]
	Primary tar mixture/bio-oil	70%	[31]
	Primary tar mixture/bio-oil	60–90%	[66]
Ferrous metal oxides			
Clay			
Palygorskite	Acetic acid	55%	[67]
Attapulgite	Acetic acid	55%	[68]
Char			
Biochar	Acetic acid	10–90%	[69]
Biochar	Primary tar mixture/bio-oil	70%	[70]
FCC			
Zeolite	Acetic acid	70–90%	[71]
Zeolite	Primary tar mixture/bio-oil	25–35%	[72]
Ash			
Coal ash	Acetic acid	55–90%	[73]
Coal ash	Acetic acid	30%	[74]
Activated alumina	Acetic acid	60%	[63]
	Acetic acid	0–60%	[29]
Noble metal			
Pt-, Rh-, Pd-/Al <sub>2</sub> O <sub>3</sub>	Acetic acid	80%, 96%, 77%	[59]
Rh-, Ru-, Pd-/Al <sub>2</sub> O <sub>3</sub>	Acetic acid	97%, 38%, 37%	[75]
Rh/La <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub>	Acetic acid	90–100%	[22]
Pd/Fe <sub>2</sub> O <sub>3</sub>	Acetic acid	100%	[23]
Transition metal			
Ni-, Co-/Al <sub>2</sub> O <sub>3</sub>	Acetic acid	100%, 100%	[25]
Ni/Al <sub>2</sub> O <sub>3</sub>	Acetic acid	100%	[26]
Ni/Al <sub>2</sub> O <sub>3</sub>	Acetic acid	100%	[27]
Ni/CeO <sub>2</sub> /ZrO <sub>2</sub>	Acetic acid	50–100%	[28]

#### 4. Conclusions

Tar represents one of the biggest bottlenecks in biomass conversion via gasification. Therefore, the goal of this study was to evaluate in a lab-scale reactor the ability of olivine, dolomite and a metal-based catalysts to reform acetic acid and its thermal decomposition products using simulated biosyngas as gas carrier. Upon heating biosyngas containing acetic acid above 400 °C, the tar is at least partially converted to higher molecular weight compounds and carbonaceous particles that will reach the reforming catalyst where they can affect the reactor performance. The tests performed assess the reforming ability of the catalysts under conditions representative of the high temperature gas cleaning unit designed by TU Delft to connect a 50 kW updraft gasifier with a solid oxide fuel cell in the EU funded project “FlexiFuel-SOFC”. The catalyst performance was evaluated assessing the outlet gas composition, the outlet tar concentration, and presence of carbonaceous deposits on the catalyst.

Initially olivine appeared able to completely convert acetic acid into non-condensable gases. However, a considerable amount of carbonaceous deposits was found on the catalyst, and the catalytic activity of olivine decreased in time, as indicated by the increasing amounts of hydroxyacetone measured. Dolomite showed promising performances at 680–750 °C since acetic acid was completely converted into non-condensable gases and only a minor amount of carbonaceous deposits was found on the low temperature part of the bed. The carbonaceous deposits accumulation was suppressed by increasing the operating temperature and the steam flow rate. However, operating dolomite at 900 °C, or pre-treating dolomite by calcination at 800 °C, causes the catalyst to become excessively brittle, which leads to powder entrainment in the gas flow, or even reactor clogging. The metal-based catalyst out-performed the naturally-occurring catalysts since it completely reformed acetic acid and suffered almost no carbonaceous deposits

accumulation. The metal-based catalyst showed good catalytic activity towards the reverse water gas shift reaction and methane reforming, while both dolomite and olivine showed some minor catalytic activity towards the reverse water gas shift reaction, but neither dolomite nor olivine showed activity towards methane reforming. The results presented are expected to assist in the development of systems based on biomass gasification, such as biomass gasifier SOFC systems.

#### Acknowledgment

This research was partially supported by the project “FlexiFuel-SOFC”. The project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 641229.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2021.105982>.

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