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Operating experience with chemical looping combustion in a 120kW dual circulating fluidized bed (DCFB) unit

Philipp Kolbitsch*, Tobias Pröll, Johannes Bolhar-Nordenkampf, Hermann Hofbauer

Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria

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Abstract

In this study, first operating experience with a 120kW chemical looping pilot rig is presented. The dual circulating fluidized bed reactor system and its auxiliary units are discussed. Two different oxygen carries, i.e. ilmenite, which is a natural iron titanium ore and a designed Ni-based particle, are tested in the CLC unit. The pilot rig is fueled with H_2, CO and CH_4 respectively at a fuel power of 65-145kW. High solids circulation, very low solids residence time and low solids inventory are observed during operation. Due to the scalability of the design concept, these characteristics should be quite similar to those of commercial CLC power plants. Ilmenite shows a high potential for the combustion of H_2 rich gases (e.g. from coal gasification with steam). The H_2 conversion is quite high but there is still a high potential for further improvement. The Ni-based oxygen carrier achieves the thermodynamic maximum H_2 and CO conversion and also very high CH_4 conversion. A variation of the air/fuel ratio and the reaction temperature indicates that the Ni/NiO ratio of the particle has a high influence on the performance of the chemical looping combustor.

Keywords: Carbon capture; Chemical Looping; Scale-Up; Gas-Solids Reactor; Fluidized Bed Systems

1. Introduction

The increasing content of carbon dioxide in the atmosphere that very likely contributes to climate change has lead to great concerns [1]. Beside other sectors, the combustion of fossil fuels has its share on the global CO_2 production and measures have to be taken to reduce these emissions. The increase of the efficiency of thermal power plants and the increased used of renewable energy sources are two ways to reduce emissions. Separation and sequestration of the produced CO_2 is third mid-term strategy and could be done in different ways. Besides pre-combustion capture, post-combustion capture and oxy-fuel combustion, the unmixed combustion represents a fourth possibility for carbon capture [2]. Therein, air and fuel are not mixed and therefore costly and energy intensive gas separation units can be omitted. Solid oxide fuel cells (SOFC) and chemical looping combustion (CLC) contribute to this group.

CLC is a novel combustion technology with inherent CO_2 separation. A CLC reactor system consists of two separate reactors, an air reactor (AR) and a fuel reactor (FR). An oxygen carrier (OC) that transports the necessary

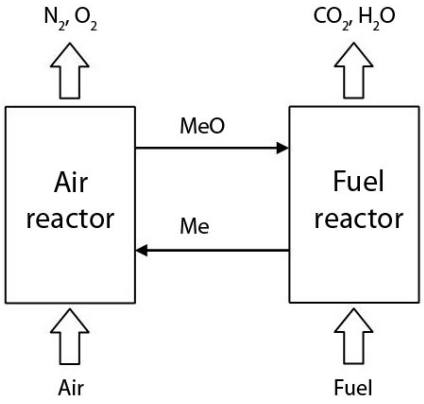

Figure 1: Chemical looping combustion principle

oxygen for combustion circulates between the two reactors (see Figure 1). In the fuel reactor the gaseous fuel is oxidized OC according to

$$H_2 + MeO_\alpha \leftrightarrow H_2O + MeO_{\alpha-1} \tag{1}$$

$$CO + MeO_\alpha \leftrightarrow CO_2 + MeO_{\alpha-1} \tag{2}$$

$$C_xH_y + (2x + \frac{y}{2})MeO_\alpha \leftrightarrow xCO_2 + \frac{y}{2}H_2O + (2x + \frac{y}{2})MeO_{\alpha-1}. \tag{3}$$

Ideally, the FR exhaust gas consists of CO_2 and H_2O only. Therefore, CLC represents a high potential CO_2 capture technology. After being (partially) reduced, the OC is transferred back to the AR where it is again (partially) oxidized according to

$$O_2 + 2MeO_{\alpha-1} \leftrightarrow 2MeO. \tag{4}$$

Depending on the active metal of the OC and the fuel, the FR is slightly exothermic or endothermic [3]. The AR is always strongly exothermic.

Different active metals have been proposed in literature for the use in CLC. These are Ni [4-8], Fe [4,8-12], Cu [4,5,13,14], Co, Mn [15] and Cd. Besides high reactivity and strength against attrition, the OC should have a high availability, low price and only little environmental impact. Since none of the stated metals features all desired properties a trade-off has to be found. The combination of different active metals (mixed oxides) is also discussed (e.g. Cu-Ni [16], Co-Ni [17], Ni-Fe [18]). In contrast to fabricated particles natural minerals, such as iron ores or ilmenite (iron titanium compound), have a lower reactivity but also a very low price.

2. Experimental

2.1. Dual circulating fluidized bed (DCFB) reactor system

Since gas-solids contact and solids transport between the reactors is very important in CLC, the AR and FR are designed as fluidized bed reactors. Lyngfelt et al. [19] have proposed a reactor system that consists of a fast fluidized bed AR and a bubbling fluidized bed (BFB) FR (see Figure 2). A very similar design is described by Ryu et al. [20]. In contrast to this design, in the DCFB reactor system (see Figure 3) the FR is operated in the turbulent regime. This way, the gas-solids contact in the FR is increased and the possible bypass of fuel in the bubble phase is reduced. Compared to other interconnected circulating fluidized beds such as described by Paisley et al. [21] and Andrus [22], in the DCFB system the global solids circulation rate is only dependent on the AR fluidization.

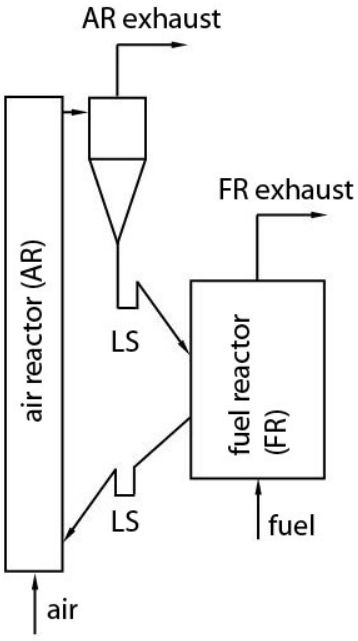

Figure 2: BFB reactor system setup as described by Lyngfelt et al. [19] and Ryu et al. [20]. The AR is designed as fast fluidized bed; the FR as bubbling fluidized bed.

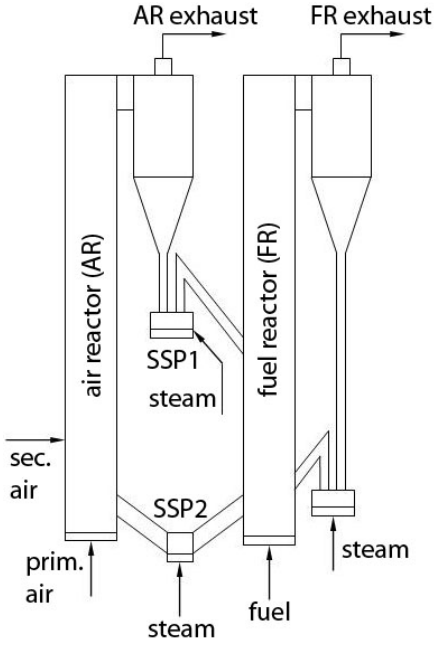

Figure 3: DCFB reactor system setup. Both, AR and FR are designed as circulating fluidized beds. Solids can be entrained at two positions in the pilot rig (SSP1 and SSP2).

Therefore, the FR can be optimized towards fuel conversion without attention to oxygen carrier circulation. Due to the direct hydraulic link in the bottom part of the reactor system (lower loop seal) the global solids hold up is inherently stabilized. Compared to the BFB FR, gas-solids contact is increased and the reactor volume is decreased (i.e. low solids inventory). This reactor design also features a high potential for scale-up.

2.2. 120kW CLC pilot rig setup

In this study first operating results with the DCFB reactor system for chemical looping combustion at Vienna University of Technology are presented. This pilot rig is designed for 120kW fuel power and a Ni-based OC. The pilot rig can be fueled with natural gas or designed mixtures of CH_4, CO, H_2 and C_3H_8. The AR is designed as a fast fluidized bed with pneumatic transport of the solids. After (partial) oxidation, the solids are entrained in the AR, separated in a cyclone separator and led to the FR via a loop seal. The offgas from the AR is cooled and analyzed. In the FR, which is designed as a fluidized bed in the turbulent regime, the gaseous fuel is oxidized in presence of the oxygen carrier. The entrained particles from the FR are separated in a cyclone separator and directed back to the FR via a loop seal in the downcomer (internal loop). The offgas from the FR is also cooled and analyzed. The direct hydraulic link in the bottom zone of both reactors closes the global solids loop of the reactor system. Unfortunately, the AR and FR height is limited by the surrounding laboratory. Due to the relatively low gas residence time in the reactors, some influence on the gas conversion compared to larger reactors is expected. The design of the fluidized bed is presented more in detail elsewhere [23]. Cold flow model results have been summarized by Pröll et al. [24].

Compared to other existing CLC pilot rigs, this unit features very high solids circulation rate with low solids inventory. This implies low particle residence time in both reactors and a very narrow age distribution of the particles. These characteristics should be very similar to commercial power plants and therefore the obtained results should reflect the performance of commercial power plants to some extent.

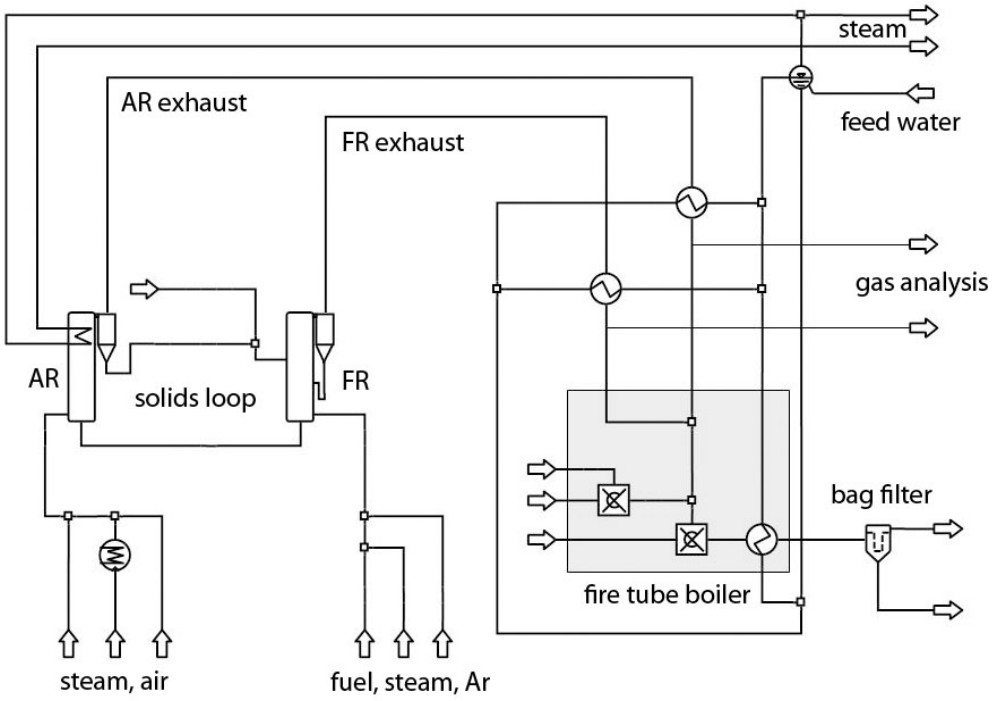

Figure 4: Arrangement of CLC reactor and auxiliary units of the 120kW CLC pilot rig at Vienna University of Technology

In addition to gas analysis, solids can be sampled at two different positions of the pilot rig (SSP1 and SSP2 in). These positions represent the solids inlet and outlet of the FR. The solids sampling procedure and results of the solids conversion determination for a Ni-based oxygen carrier have been presented by Kolbitsch et al. [25].

A process flow diagram of the whole pilot rig setup is shown in Figure 4. Beside the reactor system itself, the pilot rig is equipped with heat exchangers for the AR and FR offgases and for external AR cooling. Prior to the stack, a fire tube boiler for post combustion and a bag filter for the separation of entrained particles are arranged.

3. Results and discussion

For the evaluation of the results, the fuel conversion and the CO_2 yield are introduced. The conversion of the gaseous substance i (CH_4, H_2) is defined as

$$X_i = 1 - \frac{\dot{n}_{i,out}}{\dot{n}_{i,in}} \tag{5}$$

with the inlet and outlet molar flow n of the substance i. The CO_2 yield describes the selectivity of the reactions towards CO_2 and is calculated from the carbon balance:

$$\gamma_{CO_2} = \frac{x_{CO_2}}{x_{CO_2} + x_{CO} + x_{CH_4}} \tag{6}$$

A third parameter, the so called solids conversion, describes the oxidation state of the particle and is calculated from the particle molar masses in the fully oxidized, the fully reduced and the actual state:

$$X_S = \frac{M - M_{red}}{M_{ox} - M_{red}} \tag{7}$$

3.1. Solids circulation rate and particle residence time

Solids circulation between AR and FR is crucially necessary to operate a CLC reactor. The solids circulation rate in the reactor system can be determined via the change of solids conversion of the particle. Some results of this investigating are shown in Table 1. The solids sampling procedure and evaluation are described elsewhere [25]. The results clearly indicate very high solids circulation (at full load). Due to the low solids inventory in the AR and the FR the solids residence time is very short. This implies that the age distribution of the particle is very narrow (uniform solids conversion). The active solids in AR and FR compensate for less than 50% of the total solids inventory in this pilot rig. However, this ratio increases with plant size.

3.2. Ilmenite as natural oxygen carrier

Prior to the designed Ni-based oxygen carrier operation, a series of experiments with ilmenite, a natural oxygen carrier with the notation FeTiO3, as oxygen carrier is preformed. For this purpose the CLC pilot rig is fueled with H_2. Even though the used particles have a relatively large mean diameter (>200µm) they are used to test major parts of the CLC pilot rig and to gain first operating experience. The results are shown in Figure 5. The H_2 conversion is in the range of 0.90-0.95 and decreases slightly with fuel power. As already mentioned, these results are to be regarded as first results with ilmenite and have a high potential for further optimization. Beside the limiting reactor height and better suited particle size distribution, the optimization of different operating parameters of the pilot rig should increase the gas conversion. Nevertheless, these results are very promising and reveal ilmenite as a potential oxygen carrier for H_2 rich gases (e.g. from coal gasification with steam). More results obtained with ilmenite as oxygen carrier are presented within another contribution to this conference [26].

3.3. Ni-based oxygen carrier

Subsequent to these first tests with ilmenite, the pilot rig is operated with a Ni-based particle for which it was originally designed. Besides H_2, CO and CH_4 are used as fuel at a fuel power of 65-145kW. Compared to ilmenite, this OC has a much higher reactivity, especially towards CH_4. As shown in Figure 6, the H_2 and CO conversion is very high. Only in cases of very low solids inventory, the gas conversion is limited below maximum (i.e. air/fuel ratio (when < 1) and thermodynamics, respectively).

In addition, CH_4 is used as fuel. In the air/fuel ratio variation in Figure 7, one can observe decreasing CH_4 conversion with increasing air/fuel ratio. This is a very interesting phenomenon and is probably due to the increasing

Table 1: Global solids circulation rate, solids residence time and solids inventory for different operating cases. In these experiments a designed Ni-based oxygen carrier is used.

			solids circ. (AR)		active solids [kg]				solids residence time [s]				solids inv. [kg/MW]	
air/fuel ratio	power [kW]	fuel	m_S [kg/h]	G_S [kg/m²s]	AR	FR	circ.	total	AR	FR	circ.	total	AR	FR
0.829	63.6	H_2	661.8	10.4	15.7	16.6	32.7	65.0	85.4	90.3	177.9	353.6	246.9	261.0
0.895	63.0	H_2	818.8	12.9	14.5	16.6	33.9	65.0	63.8	73.0	149.0	285.8	230.2	263.5
0.932	63.3	H_2	901.8	14.2	13.8	15.6	35.6	65.0	55.1	62.3	142.1	259.5	218.0	246.4
1.014	61.5	H_2	1074.1	16.9	13.2	14.9	36.9	65.0	44.2	49.9	123.7	217.9	214.6	242.3
1.021	63.4	H_2	1172.8	18.4	12.8	14.9	37.3	65.0	39.3	45.7	114.5	199.5	201.9	235.0
1.069	64.2	H_2	1326.2	20.8	13.8	16.9	34.3	65.0	37.5	45.9	93.1	176.4	215.0	263.2
1.097	65.8	H_2	1804.1	28.4	14.1	16.6	34.3	65.0	28.1	33.1	68.4	129.7	214.3	252.3
0.836	140.2	CH_4	3433.5	54.0	9.1	15.3	40.6	65.0	9.5	16.0	42.6	68.2	64.9	109.1
0.886	140.2	CH_4	3572.3	56.2	9.1	15.8	40.1	65.0	9.2	15.9	40.4	65.5	64.9	112.7
0.977	138.1	CH_4	4243.8	66.7	9.3	16.9	38.8	65.0	7.9	14.3	32.9	55.1	67.3	122.4
1.064	141.5	CH_4	5067.0	79.6	8.8	18.1	38.1	65.0	6.3	12.9	27.1	46.2	62.2	127.9
1.099	143.3	CH_4	4800.0	75.5	9.8	19.4	35.8	65.0	7.4	14.6	26.9	48.8	68.4	135.4
1.093	143.4	CH_4	5615.0	88.3	10.3	19.9	34.8	65.0	6.6	12.8	22.3	41.7	71.8	138.8
1.094	143.5	CH_4	5245.0	82.4	9.8	19.0	36.2	65.0	6.7	13.0	24.8	44.6	68.3	132.4
1.087	144.4	CH_4	5390.2	84.7	9.6	19.3	36.1	65.0	6.4	12.9	24.1	43.4	66.5	133.7

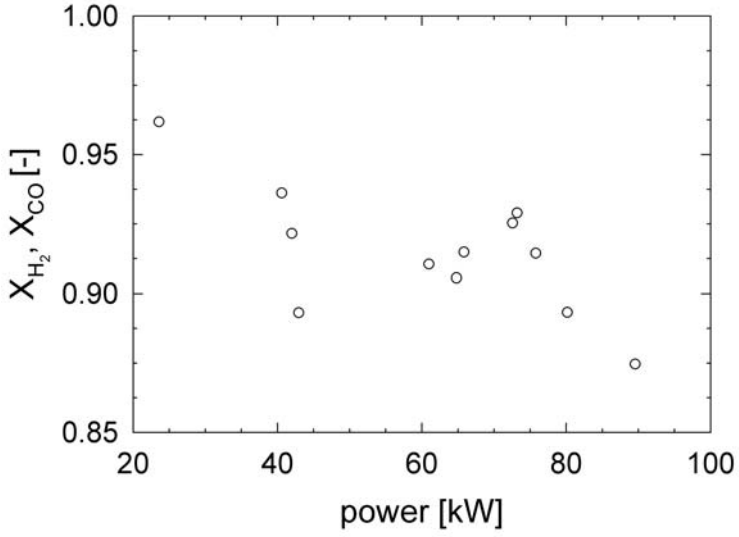

Figure 5: H2 conversion using ilmenite as oxygen carrier. The experiments are performed at 950°C FR temperature.

Ni/NiO ratio in the particle at lower air/fuel ratio (see Kolbitsch et al. [25]). The CO_2 yield strongly increases with the air/fuel ratio until enough O_2 is provided to the AR. A further increase only slightly increases the CO_2 yield. Additionally to the air/fuel ratio variation, the FR temperature is varied in Figure 7. The CH_4 conversion is promoted by a higher FR temperature but reaches a maximum at approx. 900°C. Afterwards the CH_4 decay decreased which is probably again due to a change of the Ni/NiO ratio in the particle (see Kolbitsch et al. [25]). The CO_2 yield is always promoted by higher reaction temperatures. More results with Ni-based oxygen carriers in the 120kW pilot rig are summarized by Bolhar-Nordenkampf et al. [27].

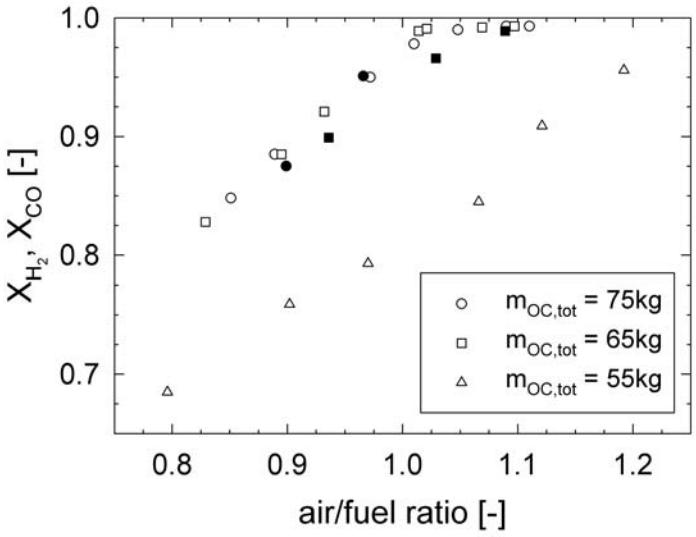

Figure 6: H_2 (○) and CO (●) conversion using a Ni-based oxygen carrier at 850-900°C.

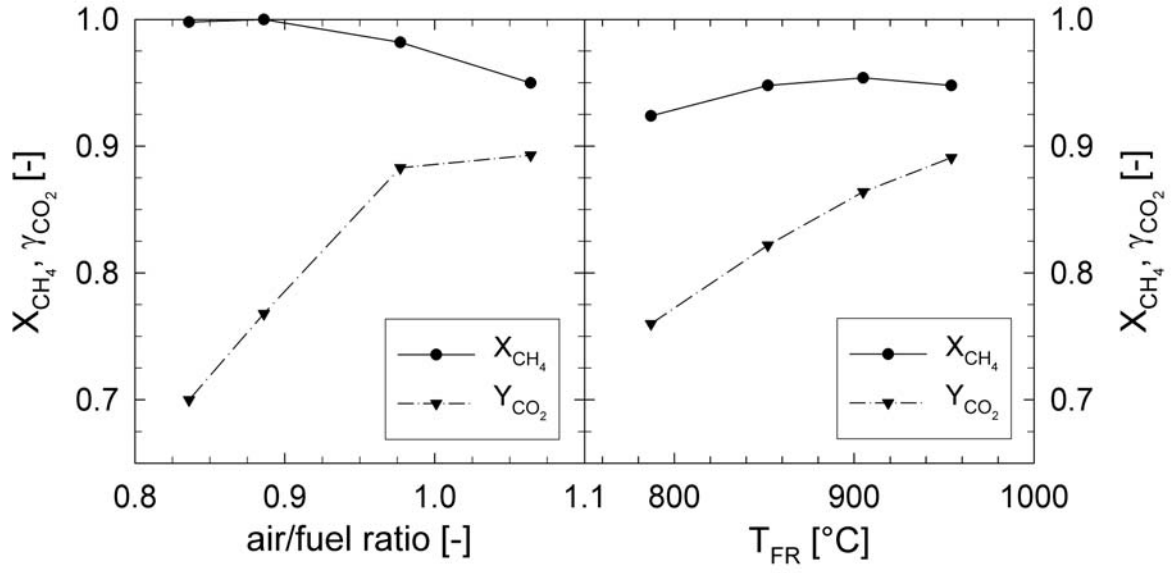

Figure 7: CH_4 conversion and CO_2 yield using a Ni-based oxygen carrier.

4. Conclusions

The 120kW chemical looping combustion pilot rig at Vienna University of Technology has been successfully put into operation. The unit is designed for natural gas and mixtures of CH_4, CO, H_2 and C_3H_8 as fuel and is operated with different oxygen carriers. High solids circulation is achieved for low solids inventories. The low solids residence time implies very narrow age distribution of the particles. Commercial CLC power plants are likely to feature two fast fluidized bed reactors. Therefore, the results obtained can be assigned to large plants to some extent. First experimental results with a natural oxygen carrier (ilmenite, $FeTiO_3$) and H_2 as fuel show very promising results. Even though the mean particle diameter of the oxygen carrier is rather high (>200μm), high gas conversion is observed. However, these results have still a high potential for optimization. The ilmenite results are then compared with the performance of a fabricated Ni-based oxygen carrier. This particle achieves thermodynamic maximum H_2 conversion when the solids inventory is sufficiently high. During operation with natural gas as fuel, high CH_4 conversion and CO_2 yield are observed. The effect of temperature and air/fuel ratio is determined and discussed.

Acknowledgments

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