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EXPERIMENTAL STUDY ON REFORMING ACTIVITY AND OXYGEN TRANSFER OF FE-OLIVINE IN A DUAL CIRCULATING FLUIDISED BED SYSTEM

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ABSTRACT

Fe-olivine was investigated in a dual circulating fluidised bed reactor system with focus on hydrocarbon reforming activity and effects of oxygen transfer. H₂, CO₂, CH₄ and 1-methylnaphthalene were fed as a surrogate gas mixture to the reforming part. Oxygen transport was developed by solids circulation. Tar decomposition was marginally affected by partial oxidation. The overall degree of tar decomposition was found to be in the range of 70 to 80%.

INTRODUCTION

Biomass gasification is a suitable option for syngas generation and is the only renewable carbon source for partial substitution of fossil fuels. Fluidised bed processing is a common technology for the conversion of solid fuels into product gas and therefore is the pre-process for direct use (heat and power supply) or for further conversion processes into synthetic natural gas, liquid fuels or other chemicals. The catalytic approach to biomass gasification, related to the reforming of hydrocarbons (tars), is widely considered and under investigation by several groups (i.e. Kiennemann et al., Corella et al. or Simell et al.) and is specified within this section. Generally, catalysts can be grouped into natural or synthetic materials. Comprehensive reviews on catalysts in biomass gasification are given by Dayton (1) and Yung et al. (2). Natural olivine is often applied as bed material in fluidised bed gasification. Several investigations have been performed focusing the catalytic properties of olivine in terms of reforming of hydrocarbons or the gasification of biomass. Comprehensive investigations have been published by Devi et al. (3), Abu el Rub et al. (4), Kuhn et al. (5), Constantinou et al. (6), Rapagna et al. (7) or Rauch et al. (8). Generally, the studies outline that olivine acts as a catalyst. It is assumed that the catalytic property is associated with pre-treatment and iron content of the particle surface. Thus, it is supposed that iron is responsible for the catalytic activity. Pecho et al. (9) studied olivine and emphasised the oxygen transfer capability and reforming activity by means of toluene. Beyond these applications, iron is usually applied as a catalyst in the chemical industry (Fischer-Tropsch synthesis, ammonia synthesis). However, the latter studies were carried out at lab-scale and

non-application oriented facilities. Thus, predictive or general statements with regard to industrial application are rather limited. The present study focused on the investigation of iron-supported olivine (Fe-olivine) to elucidate the effect of iron in terms of tar reforming. Further, it is aimed to apply Fe-olivine as an in-bed catalyst, for fluidised bed biomass steam gasification, as the iron material is considered to be active for tar reforming. The investigations were carried out at a dual circulating fluidised bed reactor system with 120 kW fuel power to consider application-oriented aspects. A previous experimental study with natural olivine in terms of hydrocarbon reforming activity and oxygen transfer was carried out by Koppatz et al. (10).

EXPERIMENTALS

Natural olivine (silicate tetrahedra with iron and magnesium) was used as the carrier material for synthesis of the iron catalyst. The natural olivine ($Mg_{1-x}Fe_x)_2SiO_4$ ($x \sim 8$ wt.-%) was provided by Magnolithe GmbH (Austria). Thermal pre-treatment of the raw material was carried out by the manufacturer in order to dry the water of crystallization. Through the pre-treatment process, the bulk material passes through a rotary kiln for approximately 4 h at 1600°C . Thus, sintering of the material was further caused by the high temperature treatment. The Fe-olivine was developed by the University of Strasbourg (Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse). The material was synthesised with 10 wt.% at a large scale by wet impregnation with iron nitrate solution. Drying of water excess (at 100°C) and calcination (at 1000°C) of the material were carried out. Thus, the final global iron content was at about 20 wt.% considering that the major part of the iron was available at the particle surface. Preparation and characterisation of Fe-olivine has been detailed by Virginie et al. (11). Moreover, Virginie et al. (12) studied Fe-olivine as a catalyst for toluene steam reforming (at a micro-reactor scale) and found high toluene conversion (95%). The study assumed that metallic iron was responsible for the high conversion rates, since catalyst reduction with H_2 was carried out as the pre-treatment step.

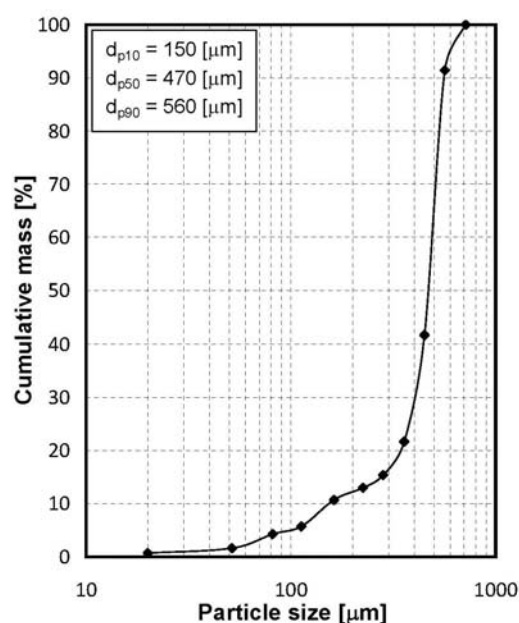


Fig. 1. Particle size distribution

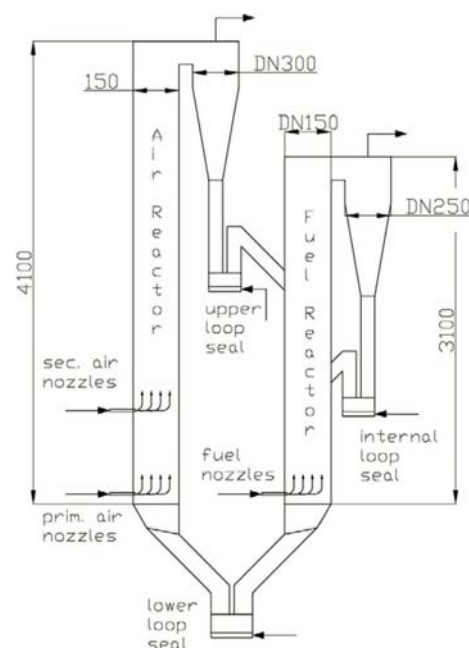
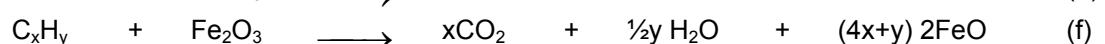
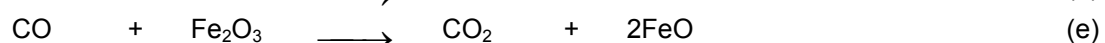
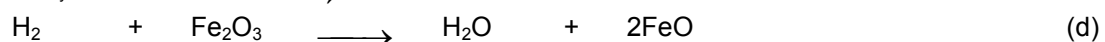
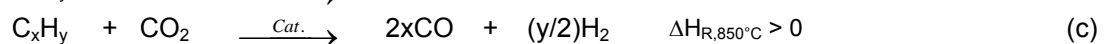
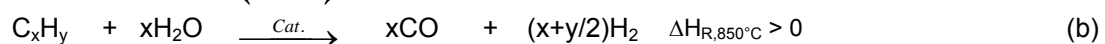
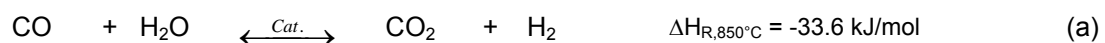


Fig. 2. Sketch of the dual circulating fluidised bed reactor system

Further, natural olivine is a non-porous material with a BET surface area of $< 0.5 \text{ m}^2\text{g}^{-1}$ is reported Devi et al. (3), but has due to its hardness of 6.5 – 7.0 on the Mohs scale a high attrition resistance. Besides mechanical stability, high availability at low cost makes the olivine advantageous for fluidised bed applications. The cumulative size distribution of the applied Fe-olivine particles is depicted in Fig. 1. According to the Geldart particle classification, the applied Fe-olivine is classified as Geldart group B. The DCFB pilot rig consists of two interconnected circulating fluidised bed reactors, named the fuel reactor (FR) and the air reactor (AR), allowing continuous circulating of solid material between the reactors. A sketch of the reactor system with dimensional information is displayed in Fig. 2. The pilot rig (nominal fuel power of 120 kW) was developed for chemical looping combustion or chemical looping reforming processes for gaseous fuels with a focus on scalability to large scale application, whereas the circulating solids act as an oxygen carrier or reforming catalyst. Further, sensitive heat transfer between the reactors is enabled by the circulating bed material. The AR is designed as a fast fluidisation regime and the FR for a turbulent fluidisation regime. Mixing of the gas phases is avoided by steam or nitrogen fluidised loop seals. Downstream of each reactor, gas and solids are separated in cyclone separators. After solid separation, the gas streams pass a common post combustion chamber equipped with a support burner for complete combustion. The exhaust gas stream is cooled down, cleaned in a bag filter and sent to the chimney. The pilot rig and further auxiliary units are detailed by Kolbitsch et al. (13) or Pröll et al. (14). For determination of fuel reactor exhaust gas concentrations, a Rosemount NGA 2000 is used and, additionally, an online gas chromatograph (Syntech Spectras GC 955) allows for cross-checking of carbon species and determination of the N_2 content for evaluation of possible gas leakages from the air reactor to the fuel reactor. The air reactor exhaust stream is analysed using a Rosemount NGA 2000. Tar measurement was carried out to determine the tar concentration and tar conversion, respectively. The tar measurement method is based on the tar protocol given by Neeft et al. (15). Further details are given by Pfeifer (16). The combustion of propane in the AR serves as the heat source to cover the heat demand in the FR whose global reaction is endothermic. Generally, the gaseous species in the FR undergo CO-shift and reforming reactions, Reactions (a) – (c).



In parallel to the gas-gas reactions, CO, H_2 or C_xH_y may be oxidised through partial oxygen input by the oxygen carrier, Reactions (d) – (f). The oxidation-reduction chemistry of iron is lumped into the formal expression FeO (Fe_{II}) and Fe_2O_3 (Fe_{III}), Reaction (g). The air reactor was fuelled with propane (C_3H_8) and air. A surrogate gas mixture of H_2 (52 vol.%), CO_2 (40 vol.%) and CH_4 (8 vol.%) was fed into the FR. The surrogate gas mixture is related to product gas derived by steam gasification of biomass, assuming that CO and H_2O are formed in the FR, Reaction (a).

1-Methylnaphthalene (1-MN) was added as a tar model compound to the FR gas feed. Thus, a strong reducing atmosphere developed in the FR. The AR was alternately operated at stoichiometric air/fuel ratios (λ_{AR}) > 1 and < 1 , resulting in O_2 or CO excess in the AR exhaust gas. Fig. 3 displays the experimental matrix.

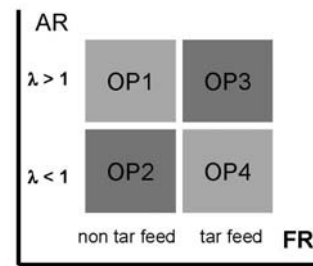


Fig. 3. Experimental matrix

RESULTS AND DISCUSSION

Fluid Dynamic Characteristics

Fig. 4 displays the pressure profile of the reactor system, which was about the same for all the operation points. Due to the application of coarse particles compared to the conventional particle size for circulating fluidised risers and the design particle size of the DCFB reactor system, the exponential decay of pressure in the air reactor was less developed. The pressure profiles (AR and FR) indicate the decrease of solid concentration and the increase of voidage with reactor height, respectively. A low solid circulation developed in the AR. For the FR, a high solid concentration was found in the bottom region and the upper part was lean in solids. Fig. 5 highlights the mapping of the fluidisation regime according to the map suggested by Bi and Grace (17). The AR was operated slightly above the terminal velocity with superficial gas velocity of ~ 4.5 m/s. A bubbling fluidised bed developed in the FR with a U/U_{mf} ratio (superficial velocity/minimum fluidisation velocity) of 7 – 8 at a superficial gas velocity of ~ 3.5 m/s.

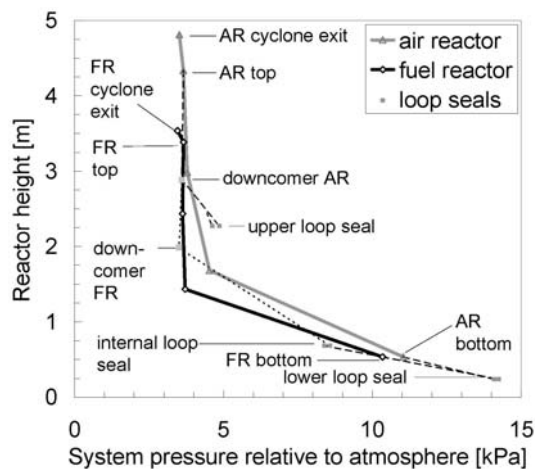


Fig. 4. Pressure profile in the reactor system

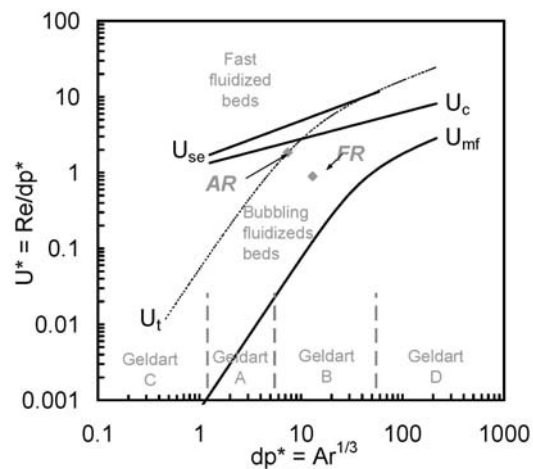


Fig. 5. Fluidisation regime of FR and AR according to Bi and Grace (17)

Reaction and Conversion Behaviour

The mean residence time in the FR amounted to ~ 3 s. Further, the FR operated at a mean gas hourly space velocity (GHSV) of ~ 1350 h^{-1} . The FR exhaust gas composition for OP1 to OP4 is highlighted in Fig. 6.

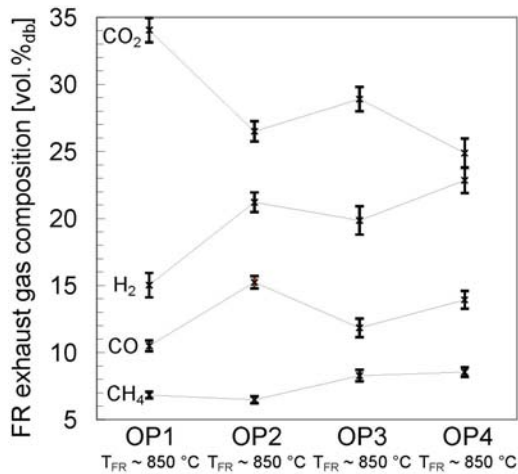


Fig. 6. FR exhaust gas composition, mean values and standard deviation of measurement

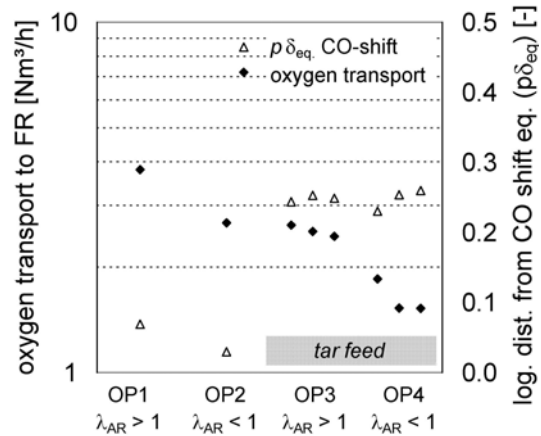


Fig. 7. Mapping of oxygen transport and gas conversion (logarithmic deviation from CO-shift equilibrium)

Due to nitrogen fluidisation of the loop seals and argon flushing of the pressure measurements, the FR exhaust gas stream was diluted by about 25 vol.%_{db}. OP1 was taken as the benchmark point and was characterised by highly developed oxygen transfer. The restricted oxygen transport which developed in OP2 (AR operation with CO excess) resulted in a considerably different exhaust gas composition compared to OP1, see Fig. 6. CO and H₂ were partially oxidised towards CO₂ and H₂O. Compared to OP1, the CO content increased to about 45% and the H₂ content increased to about 41% during OP2. The shift in CO, CO₂ and H₂ indicates partial oxygen transfer with selectivity towards the oxidation of CO and H₂. The content in CH₄ was marginally influenced. Tar feed (13.3 g/Nm³) was performed within OP3 at $\lambda_{AR} > 1$. The feed of the tar compound (C₁₁H₁₀) caused a shift in gas composition, since the total input in carbon and hydrogen increased. Based on OP1, the content of H₂, CO and CH₄ increased. The content in CO₂ decreased, since the relative amount of oxygen was lowered by the hydrocarbon feed. However, the gas composition was further affected by the overall reaction behaviour and the solids. Limited oxygen transfer developed in OP4 (AR operation with CO excess). Hence, the partial oxidation of CO and H₂ was disabled. Thus, the relative contents in CO₂, CO and H₂ shifted. Evaluation of process data using a data reconciliation method for fulfilment of mass and energy balances was carried out, Bolh ar-Nordenkampf et al. (18). Thus, the oxygen transfer in the reactor system is specified. Further, the logarithmic deviation from CO-shift equilibrium was determined to rate the gas conversion, Eq. (1).

$$p\delta_{eq}(p_i, T) = \log_{10} \left[\frac{\prod_i p_i}{K_p(T)} \right] \quad \text{Eq. (1)} \quad K_{P, CO-shift} = -1.6164 + 1.7632 \cdot \frac{1000}{T[\text{K}]} \quad \text{Eq. (2)}$$

The actually measured gas phase partial pressure of the species i is expressed as p_i . K_p is the equilibrium constant calculated from pure substance thermodynamic data as a function of temperature, according to Eq. (2), derived by (19). Oxygen transfer and deviation from CO-shift equilibrium are highlighted in Fig. 7. In each case (OP3 and OP4), three tar samples were taken. Thus, in contrast to OP1 and OP2, three values

for oxygen transfer and $p\delta_{eq}$ are given for OP3 and OP4. Thus, the values correspond to the tar sampling time. Generally, the oxygen transfer was lowered in the case of CO excess in the AR. However, the oxygen transfer was not completely inhibited. The total solid inventory has a certain quantity of oxygen available, which was present in different iron oxidation states and was released with advancing operation. Despite the substoichiometric oxygen supply (CO excess in the AR exhaust gas), oxidation of iron might occur, but at lower quantities. Furthermore, the oxygen transfer capacity decreased, since particle attrition minimised the total solid inventory. It is generally found that (Fig. 7):

- oxygen transfer (during OP2) was reduced to about 30% compared to OP1
- similar reduction comparing OP3 and OP4, but at lower quantities

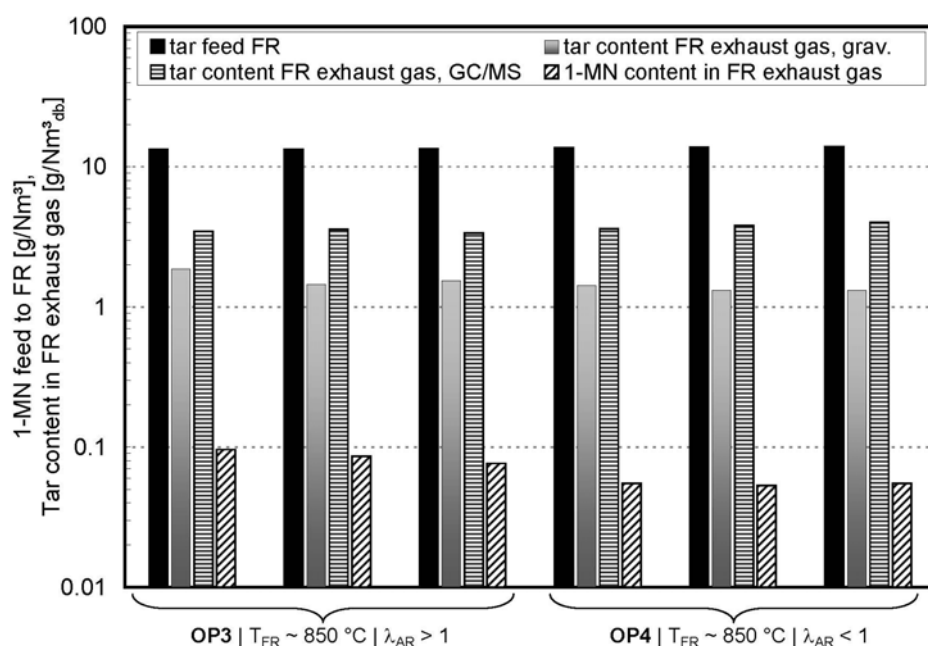


Fig. 8. Tar feed and tar measurement FR

The CO-shift was close to equilibrium for OP1 and OP2 (Fig. 7), but showed minor values above zero. Hence, the actual state of the exhaust gas composition was slightly on the side of the products, Reaction (a). Lower oxygen transport (OP2) resulted in a shift towards the equilibrium state. Thus, the oxidation caused by oxygen transfer dominated the product side of the CO-shift reaction (CO₂ content increased). Considerable deviation in CO-equilibrium was found for the operation points with tar feed. The shift from the equilibrium state proceeded towards the product side (CO₂ and H₂), ($p\delta_{eq} \sim 0.25$, deviation of about 75%). The results of tar measurement (three measurements per operation point) are summarised in Fig. 8. The graph depicts the amount (logarithmic scale) of tar compound feed (1-MN), the residual tar content in the FR exhaust gas (according to GC/MS and gravimetric method) and the content of 1-MN (unconverted part) in the FR exhaust gas. The tar feed ranged from 13.3 to 13.9 g/Nm³, due to fluctuation of the pumping system. 1-MN was converted to about 99%, since residual contents of 1-MN below 0.1 g/Nm³_{db} were measured. Certain hydrocarbons were subject to re-combination. Thus, heavy tars (GC/MS undetectable) were formed. The mean gravimetric tar content for OP3 was about 1.6 g/Nm³_{db}. A lower content of about 1.3 g/Nm³_{db} was found for OP4 with

a decreasing tendency during the operation point. The amount of GC/MS detectable tars ranged from 3.5 to 4.0 g/Nm³_{db}. Hence, the conversion amounted to roughly 73%. The major part (~94 wt.%) of the GC/MS detectable tars was naphthalene (C₈H₁₀). The minor part (~6 wt.%) consisted of intermediate products of decomposition (1H-indene, 1-benzothiophene, acenaphthylene and 2-methylnaphthalene).

CONCLUSION

The investigation focused on the reforming activity (tar conversion) and influence of partial oxygen transfer. A surrogate gas mixture with 1-Methylnaphthalene as a model tar compound (related to the product gas derived by biomass steam gasification) was exposed to the catalytically active material Fe-olivine. Thus, the performance was studied under ash, chlorine and sulphur-free conditions. It was found that the catalyst acted as an oxygen carrier. It was assumed that Fe_{III} (hematite) was reduced to Fe_{II} (wustite) in the FR. However, Fe₃O₄ (magnetite) might occur as part of the reduction-oxidation chemistry. The oxygen transfer to the fuel reactor was influenced by modification of the air reactor operation (O₂ or CO excess in the air reactor exhaust gas). Complete prevention of oxygen transfer was not achieved, since the total solid inventory possessed a certain quantity of oxygen which was bound as iron oxides and was not entirely reduced during the operation time. Further, iron oxidation occurred unavoidably to a certain quantity, due to contact of the solids with the oxygen-containing fluidisation agent (propane and air). However, it was found that CO and H₂ were oxidised towards CO₂ and H₂O, respectively. The oxidation selectivity was highly developed towards CO and H₂, since it was found that tar reduction was marginally influenced by partial oxidation. The 1-MN was decomposed to 99 wt.%. However, full hydrocarbon decomposition was not achieved, since further hydrocarbons were generated by recombination. The tar conversion based on GC/MS measurement was approximately 73%, containing mostly naphthalene. Naphthalene is a representative of aromatic ring hydrocarbons and is therefore difficult to open due to the bonds of the aromatic rings. Hence, the catalyst activity was classified in the medium to high range. It is suggested that the iron did not act as a CH₄ reforming catalyst, but CH₄ was a product of tar conversion. The overall hydrocarbon reforming capacity of Fe-olivine might be influenced by the occurring iron state at the particle, since it has been reported by Nordgreen et al. (20) and Virginie et al. (12) that metallic iron is obviously active in reforming and cracking. Thus, a further activity upgrade is might be achieved (i.e. long term behaviour). Moreover, the Fe-olivine catalyst featured the CO-shift equilibrium. This aspect is corroborated by the findings of Rhodes et al. (21), who reported that iron oxide is a catalyst for CO-shift.

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NOTATION

AR	air reactor	$p\delta_{eq}$	logarithmic deviation from equilibrium
FR	fuel reactor	λ	stoichiometric air/fuel ratio

1-MN	1-Methylnaphthalene	K_p	equilibrium constant
U	superficial velocity, [m/s]	p_i	partial pressure of gas species i
U_{mf}	minimum fluidisation velocity, [m/s]	U_{se}	superficial velocity at border between turbulent and fast fluidisation, [m/s]
U_t	terminal velocity, [m/s]	U_c	superficial velocity at border between bubbling and turbulent regime, [m/s]

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