Process activated ilmenite as catalyst for cleaning of biomass producer gas

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Background

Biomass gasification into a gaseous fuel is a promising technology for reducing the CO_2 emissions and the dependency on fossil fuels. The raw gas produced mainly consists of permanent gases such as H_2, CO, CO_2, CH_4, and light hydrocarbons but also an unacceptable amount tars that need to be mitigated to further upgrade the gas. Hot gas cleaning using catalysts is particularly attractive. With this technique, not only the tar concentration in the producer gas is reduced, but the gas composition can also be adjusted.

In contact with the raw gas, the metal oxide catalyst Me_xO_y is reduced through the combustion of hydrocarbons C_iH_j, CO and H_2 available in the raw gas , (1). As the oxidized oxide Me_xO_y is reduced to Me_xO_{y-1}, it will act as a catalyst for light hydrocarbons/tar C_nH_m reforming with the reforming media H_2O^* and CO_2^* (2). In addition to these reactions, carbon can also be formed and deposited on the particles. In the high steam content environment, water – gas shift reaction (3) will also play a role as CO and H_2 are available in the gas mixture.

$$C_iH_j + H_2 + CO + Me_xO_y \rightarrow CO_2 + H_2O + Me_xO_{y-1} \quad (1)$$

$$C_nH_m + Me_xO_{y-1} + H_2O^* + CO_2^* \rightarrow C_iH_j + H_2 + CO + Me_xO_{y-1} + C \quad (2)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (3)$$

Experimental

The ilmenite ($FeTiO_3$) used here was collected in the fly–ash from the Chalmers 12 MW circulating fluidized bed boiler. The fraction used was in the range 45–90 µm. The idea was to test the catalytic ability of ilmenite towards raw gas upgrading; in particularly tar removal at the temperature of 800°C and considering three residence times (RT) for the gas in the reactor. The reactor has bubbling-bed configuration with a tubular shape, see Fig. 1, and is operated with alternating oxidizing/reducing conditions. The operating parameters are summarized in Table 1.

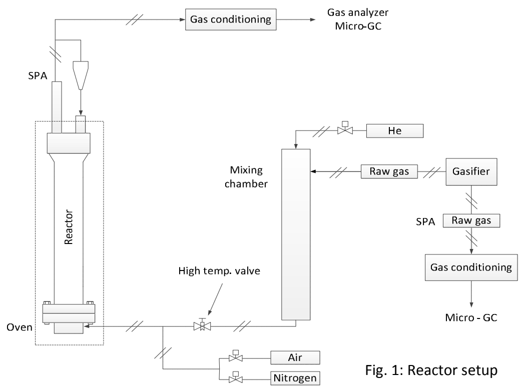

Fig. 1: Reactor setup

Operating properties	Name of experiments		
	RT 1	RT 2	RT 3
Gasifier			
Bed material		Silica sand	
Temperature (°C)		~820	
Fuel	←	Wood pellet	→
Fuel flowrate (kg/h)		~293	
Steam flowrate (kg/h)		~160	
Experiments			
Bed quantity (g)	300	300	200
Raw gas flowrate (wet) (L_n/min)	3.1	2.1	0.9
He tracing (L_n/min)	0.3	0.3	0.24
Flowrate of air/nitrogen/mixture of 10% oxygen (L_n/min)	1.5	1.5	1.2
Temperature (°C)	800	800	800
RT (s)	0.6	0.8	1.1

Table 1: Experimental conditions

Results

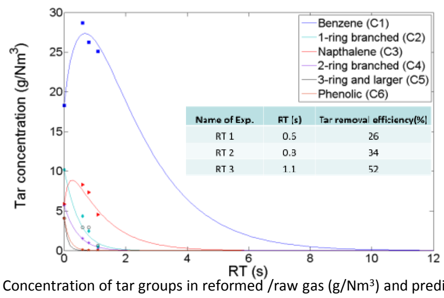

Fig. 2: Concentration of tar groups in reformed /raw gas (g/Nm³) and prediction trends

- Tar reduction up to 52% at the higher RT (gas upgrading basis).
- From a RT of 5 s, one could expect full conversion of all tars but benzene.

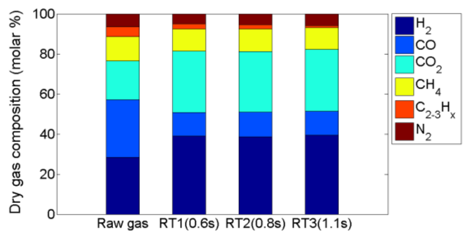

Fig. 3: Change in permanent gas composition

- The H_2/CO ratio was brought from 1 in the raw gas to almost 3, an interesting value if methanation is considered downstream.
- Nearly all $C_{2-3}H_x$ are converted at the higher RT.

Conclusions

Ilmenite fines from the Chalmers 12 MW circulating fluidized bed boiler were used as a tar reforming catalyst in a bubbling fluidized bed reactor operated at 800°C and fed with a raw gas from the Chalmers 2–4 MW indirect biomass gasifier. The reactor was operated in batch mode with alternating redox conditions to decouple the effect of oxygen transport and actual catalysis. Three levels of gas – solid contact time were investigated. Overall, the potential of using process activated ilmenite as a reforming catalyst for upgrading raw gas has been demonstrated. Moreover:

- Tar removal efficiency & tar decomposition pattern depend on the gas – solid contact time. 52% on tar-to-reformed gas basis achieved at the contact time of 1.1 s. The longer the gas – solid contact time, the higher tar removal efficiency
- The gas composition was adjusted with an H_2/CO ratio increased from approximately 1 in raw gas to slightly higher than 3 in the reformed gas
- No defluidization of the ilmenite bed was observed during the reducing raw gas operation (>80 min). Thus, high rate of particle circulation for regeneration in an up–scaled system probably is not required.
- Using ilmenite fines for secondary tar reforming of raw gas and/or in the gasifier for primary tar reforming seems possible