Modelling of the oxy-combustion fluid catalytic cracking units

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Abstract

Oxy-combustion enables the capture of CO_2 in the flue gas from fluid catalytic cracking (FCC) units. A pilot demonstration of the process was performed in the CO_2 Capture Project (CCP). Two operating modes were tested and the CO_2 was concentrated to be around 95 vol.%. This paper presents a modelling study of the process. The models are derived from literature work on the air-fired FCC units. The main modelling results such as the product yields and the flue gas compositions fit well with the experimental test. It is observed that the conversion rate has been increased by around 4.5% in the "same inert" mode (the same volumetric flow of inerts as in the air fired case) compared to the air-fired case. The reason is that the regenerator temperature is lower due to a larger heat capacity of CO_2 compared to N_2. As a result, larger catalyst to oil ratio should be used in order to maintain the reactor temperature. The study provides fundamental insights for the understanding of oxy-FCC process. The work is expected to be used as a basis for further optimization of the process.

Keywords: oxy-combustion, CO_2 capture, fluid catalytic cracking, process modelling.

1. Introduction

The fluid catalytic cracking (FCC) unit is responsible for 20-30% of total CO_2 emissions from a typical refinery (de Mello et al., 2013). Oxy-combustion, as one of the three well-known methods for CO_2 capture (i.e. post-, pre- and oxy-combustion), enables the concentration and capture of CO_2 in the flue gas from FCC units. In an oxy-FCC process, pure O_2 is used instead of air for the burning of coke in the regeneration process of spent catalyst. As a result, dilution of CO_2 with N_2 is avoided. A pilot scale demonstration of the oxy-FCC process was performed in the CO_2 Capture Project - CCP (de Mello et al., 2013). The test shows that it is technically feasible to operate an oxy-FCC unit. The CO_2 can be concentrated to 95 vol.%. Two operating modes were tested in the pilot scale plant: the "same heat" mode (the same amount of heat removed from the regenerato as in the air fired case) and the "same inert" mode (the same volumetric flow of inerts as in the air fired case). The product yields and conversion rate in the "same heat" mode are very similar to the values obtained in the air-fired base case. A higher conversion rate has been achieved when the "same inert" mode is used.

The modelling of the FCC process is a challenging task due to complex hydrodynamics and reactions involved. Considerable modelling studies have been performed on the air fired FCC process with respect to various levels of details. Most of the modelling work is based on the n-lump kinetic models that simplifies the complex reaction system where n varies from 3 to 12 or even more (Bollas, 2007). A recent study by Pinheiro et al. (2011) provides a comprehensive review. According to the author's best knowledge, modelling of the oxy-FCC process has not yet been investigated in public literature. A

distinct feature of the oxy-FCC unit is that the flue gas is mainly composed of CO_2 instead of N_2. Detailed modelling of this novel process (oxy-FCC) provides fundamental insights about the process. The modelling work is also helpful for preliminary evaluation and further optimization of the process performance with respect to energy consumption and cost related to CO_2 capture. This study attempts to develop models for the oxy-FCC process. The models are developed based on literature models on the air-fired FCC processes. The 5-lump kinetic models (Dasila et al., 2014, Dave, 2001) have been used in this study. Almost the same components in the models are presented in the CCP report (de Mello et al., 2013), it is thus convenient to validate the modelling results.

2. Process description

A typical air fired FCC unit is shown in Figure 1(a). The oil feed is converted into the desired products with the help of catalyst in the riser reactor. Coke is an undesired by-product that is accumulated on the surface of the catalyst. As a result, the catalyst gets less active and needs to be regenerated. The coke on the spent catalyst is burned with air in the regenerator and CO_2 is thus produced. The CO_2 fraction is around 10-20 vol.% in the flue gas of the regenerator (de Mello et al., 2013). The CO_2 can be concentrated in the oxy-combustion case, as shown in Figure 1(b). An air separation unit is used to remove the N_2 from the O_2 prior to combustion. As a result, the CO_2 is concentrated in the flue gas due to the absence of N_2. A portion of the flue gas (known as Recycled Flue Gas- RFG), containing mainly CO_2 and H_2O, is recycled to the regenerator for temperature control. The CO_2 has a larger heat capacity than the N_2. The heat transfer characteristics and heat balance are thus different compared to the air-fired case. Two operating modes, the "same heat" and the "same inert" modes, were thus tested in the pilot Oxy-FCC facility to infer the effect of replacing N_2 as inert in the air fired case with CO_2 as inert in the oxy fired case.

3. Process modelling

The models presented here are based on earlier published work (Arbel et al., 1995, Dasila et al., 2014, Dave, 2001). The reactor is assumed to be one-dimensional. The following 5 components are assumed to be present in the riser reactor: gasoil, gasoline, liquefied petroleum gas (LPG), dry gas and coke, which are indexed as $j = 1,2,3,4$ and 5, respectively. In total 9 possible reaction paths among these components are defined and shown in Figure 2.
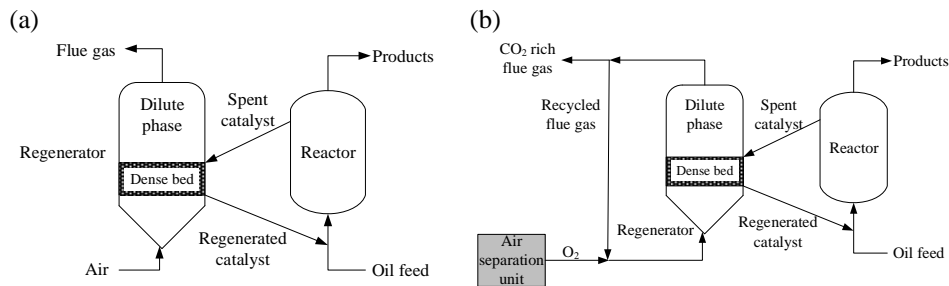

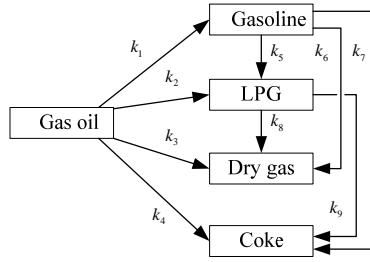Figure 1 The FCC units: (a) the air fired case, (b) the oxy-combustion case

Figure 2 Reaction paths

The regenerator is also assumed to be one-dimensional and the gas phase is assumed to be plug flow. Four main reactions (I-IV) are defined in the regenerator. Note that the combustion of CO has two parallel paths: heterogeneous (IIIa) and homogeneous (IIIb). The combustion of H_2 (reaction IV) is assumed to be complete and immediate. The regenerator is modelled based on the two-phase model: a bottom dense phase and a top dilute phase. The coke is assumed to be burned in the dense phase. The catalyst entrained and the carbon monoxide are mainly burned in the dilute phase.
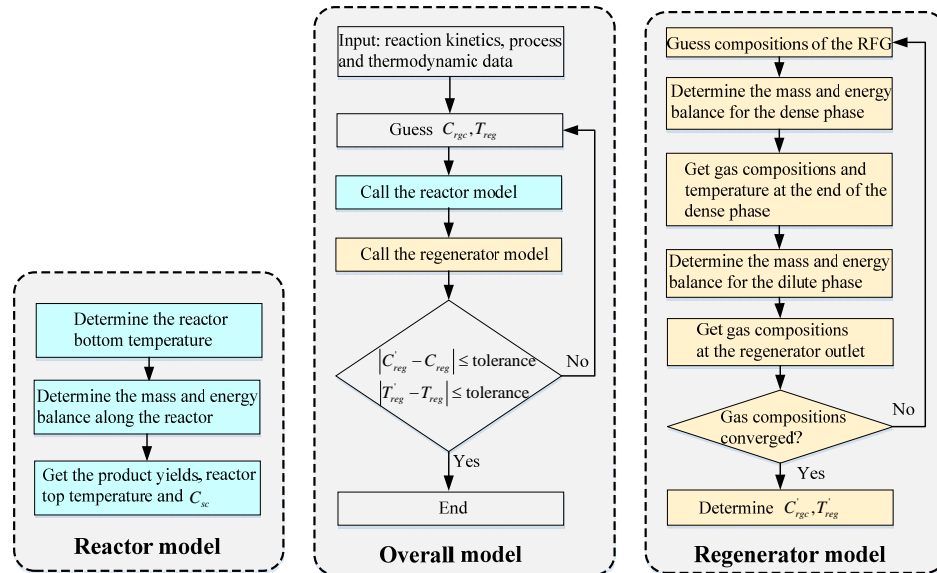
(I) $\quad C + 0.5\,O_2 \xrightarrow{k_I} CO$

(II) $C + O_2 \xrightarrow{k_{II}} CO_2$

(IIIa) $CO + 0.5O_2 \xrightarrow{k_{IIIa}} CO_2$

(IIIb) $CO + 0.5O_2 \xrightarrow{k_{IIIb}} CO_2$

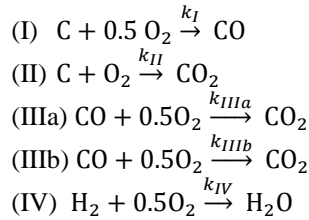(IV) $\quad H_2 + 0.5O_2 \xrightarrow{k_{IV}} H_2O$

Figure 3 The overall oxy-FCC models

Table 1. Results comparison between the modelling and experimental work

Operating mode	Experimental results (de Mello et al., 2013)			Modelling results		
	Air fired	Oxy-fired		Air fired	Oxy-fired	
		Same heat	Same inert		Same heat	Same inert
Reactor						
Temperature, ºC	540	540	540	525.6	525.6	522.3
Vacuum gasoil feed temperature, ºC	350	349	348	350	350	350
Feed flow, kg/s	0.042	0.042	0.042	32.14	32.14	32.14
Yields (mass basis), wt%		(% change relative to the air-fired case)			(% change relative to the air-fired case)	
Dry gas	3.0	-1.9	-1.6	4.4	0	7.2
LPG	14.9	2.8	6.7	15.6	0	4.5
Gasoline	43.2	-0.8	2.4	43.3	0.3	3.8
Gas oil	34.7	-	-	31.9	0	-6.2
Coke	4.2	0.8	9.0	4.9	0	7.3
Conversion rate	65.3	1.0	4.9	68.1	0	4.5
Regenerator						
Dense phase temperature, ºC	710	709	689	713.6	713.9	679.4
Air/oxidant temperature, ºC	249	249	251	249	249	249
Excess O_2 in flue gas, mol%	2.7	2.6	2.5	2.6	2.6	4.6
%O_2 in oxidant gas, mol%	21	28.9	23.8	21	29	24
Flue gas composition, mol% (dry)						
CO_2	14.2	94.3	94.8	13.0	94.1	91.7
O_2	2.7	2.6	2.5	2.6	2.6	4.6
N_2	83.1	3.1	2.5	84.4	3.3	3.2
CO	0.00	0.06	0.11	0.03	0.06	0.55

The reaction kinetic data are referred to the work by Dave (2001). For a differential height in both the reactor and regenerator, detailed mass and energy balances can be formulated. The profiles of temperature and component flows can then be determined by integrating the differential balances along the total heights. Model details are not presented here due to space limitations.

Both air-fired and oxy-fired cases are studied. The flowchart for implementing the models of the entire FCC unit is presented in Figure 3. Initial values for the coke on the regenerated catalyst (C_{rgc}) and the regenerator temperature (T_{reg}) are guessed in order to solve the reactor model. The product yields and the coke on the spent catalyst (C_{sc})

are then obtained before solving the regenerator model. In the oxy-combustion case, the compositions of the RFG should be initially guessed in order to determine the compositions of the oxidant gases at the inlet of the regenerator. An iteration procedure is used to ensure that the compositions of gases at the outlet of the regenerator are the same as the ones of the RFG. This iteration procedure is not required in the air-fired case as this recycle stream is not required. New values for the coke on the regenerated catalyst (C'_{rgc}) and the regenerator temperature (T'_{reg}) can then be obtained. An iteration procedure is necessary to ensure that C_{rgc} and T_{reg} are converged. The models are implemented with the numerical computation tool GNU Octave 4.0.0. (Eaton et al., 2015).

4. Results and discussions

The comparison between the modelling results and the pilot testing results (de Mello et al., 2013) are presented in Table 1. Both the "same heat" and "same inert" operating modes are studied for the oxy-fired case. The product yields calculated from process modelling fit well with the experimental values, particularly for the main products gasoline (14.9% vs. 15.6%) and LPG (43.2% vs. 43.3%). Although the difference in relative changes of the dry gas yield is large (-1.6% vs. +7.2%), the difference in absolute values should be negligible since the absolute value of the dry gas yield is only around 3.0%. Similar to the observations achieved in the pilot plant test, the modelling results show that the same conversion rate has been achieved in the "same heat" mode compared to the air fired case. Larger conversion rate (+4.5%) has been achieved in the "same inert" mode. The reason is that the regenerator temperature is lower due to a larger heat capacity of CO_2 compared to N_2. As a result, larger catalyst to oil ratio should be used in order to maintain the reactor temperature. The conversion rate thus increases.

The modelling results of the regenerator are also very close to the pilot testing results, particularly for the compositions of major components such as N_2 and CO_2. The "same inert" mode has the largest deviations. The molar fraction of O_2 in flue gas is higher (2.5% vs. 4.6%) in the modelling study in order to maintain the "same inert". This is the main reason why the molar fraction of CO_2 in flue gas is lower (94.8% vs. 91.7%). For the same reason, the dense phase temperature is lower (679.4 ºC vs 689 ºC) in the modelling study. The CCP report (de Mello et al., 2013) has not presented sufficient details such as the operating pressures of the reactor and regenerator. Further validation of the models can be performed as long as such details are included.

A further conditioning process of the CO_2 captured may be required depending on downstream process of CO_2. The CO_2 purity in the flue gas is related to the purity of O_2 supplied and the amount of recycled flue gas. There is a trade-off in the energy consumption of the CO_2 conditioning process and the air separation unit. The models developed in this paper are expected to be used as the basis of further optimization of the oxy-FCC process.

5. Conclusions

The oxy-combustion of coke in FCC units enables the capture of CO_2. The models for the oxy-FCC process have been investigated in this study. The 5-lump kinetic models and the two-phase models are used to describe the reactor and the regenerator respectively. The recycling of flue gas for temperature control has been included in the

model. The main results such as the product yields and the flue gas compositions fit well with the pilot test results. The CO_2 in the flue gas is concentrated to around 95 mole% (dry basis). In the "same inert" operating mode, the regenerator temperature is lower due to a larger heat capacity of CO_2 compared to N_2 and a larger catalyst to oil ratio is thus used in order to maintain the reactor temperature. As a result, the conversion rate has increased by around 4.5%. The work is expected to be used as a basis for further optimization of the Oxy-FCC process for CO_2 capture in a refinery.

Acknowledgement

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