

A Novel Approach to CO₂ Capture in Fluid Catalytic Cracking — Chemical Looping Combustion

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Abstract

Oil refineries collectively account for about 4-6 % of global CO₂ emissions and Fluid Catalytic Cracking (FCC) units are responsible for roughly 25 % of these. Although post-combustion and oxy-combustion have been suggested to capture CO₂ released from the regenerator of FCC units, Chemical Looping Combustion (CLC) is also a potential approach. In this study, the applicability of CLC for FCC units has been explored. A refinery FCC catalyst (equilibrium catalyst-ECat) was mixed mechanically with reduced oxygen carriers; Cu, Cu₂O, CoO, and Mn₃O₄. To identify any detrimental effects of the reduced oxygen carriers on cracking, the catalyst formulations were tested for n-hexadecane cracking using ASTM D3907-13, the standard FCC microactivity test (MAT). To investigate the combustion reactivity of coke with physically mixed oxidised oxygen carriers, CuO, Co₃O₄ and Mn₂O₃, TGA tests were conducted on a low volatile semi-anthracite Welsh coal, which has a similar elemental composition to actual FCC coke, with various oxygen carrier to coke ratios over the temperature range 750-900 °C.

The results demonstrated that, whereas Cu was detrimental for cracking n-hexadecane with the ECat, Cu₂O, CoO, and Mn₃O₄ have no significant effects on gas, liquid and coke yields, and product selectivity. Complete combustion of the model coke was achieved with CuO, Co₃O₄ and Mn₂O₃, once the stoichiometric ratio of oxygen carrier/coke was higher than 1.0 and sufficient time had been provided. These results indicate that the proposed CLC-FCC concept has promise as a new approach to CO₂ capture in FCC.

Keywords: CO₂ Capture, Fluid Catalytic Cracking, Chemical Looping Combustion, Oxygen Carrier.

1 Introduction

Heavy industries including cement, iron-steel, oil refining, are responsible for approximately 20% of global CO₂ emissions [1] of which oil refineries account contribute 4-6 % [1-3]. CO₂ emissions in refineries arise from a number of different processes, including Fluid Catalytic Cracking (FCC), hydrogen production, and sulphur recovery units in addition to the combustion related sources (e.g. heaters and boilers) [4]. The regenerator part of FCC unit is one of the largest CO₂ emitters, about 20-35 %, from a standard refinery [1, 4].

Based on the characteristics of the FCC process, it is possible to capture the CO₂ released from the regenerator using post-combustion capture (PCC) [5-8] where the CO₂ in the flue gas can be separated using an amine scrubbing technology. However, other processes notably oxy-combustion capture (OCC) and chemical looping combustion (CLC) potentially offer considerably lower energy penalties than PCC [9, 10]. For FCC with OCC, instead of air, oxygen mixed with recycled CO₂ is used for the combustion of coke which is deposited on the FCC catalyst during cracking [8-13]. The PCC and OCC for FCC unit have been evaluated by Miracca and Butler [8], Mello et al. [9], and Melien and Roijen [10]. Additionally, to evaluate the PCC for FCC units, an industrial case study having a capacity of 60,000 barrels per day has been considered by Digne et al [7]. The technical evaluation of these systems showed that, while the optimum CO₂ capture level for PCC is not higher than 90 % [7-10], for OCC it is about 99 % [8-10]. However, while there is no need any modification on the regenerator of FCC units for PCC, operating conditions of the regenerator must be modified for OCC technology. On the other hand, there are no significant changes in the stability of operation, the product profile, and effectiveness of coke burn [9]. The operation of FCC units with OCC is expected to be more flexible than with PCC and also requires a much smaller footprint [8]. As for the economic evaluation, due to the high air separation unit cost, the total installed cost for an OCC is calculated to be approximately 2 times higher than for a PCC unit [9]. Similarly, in another study, the total capital investment for OCC is estimated at 1.5 times higher than for PCC [10]. On the other hand, the total cost of the required chemicals for PCC was approximately 80 % higher than that for OCC. Furthermore, although PCC for FCC units had a lower capital cost [14], OCC has a lower CO₂ avoided cost [9, 10].

Although OCC is a promising technology for FCC, it still needs to be improved before commercial applications [8, 15]. A high energy penalty and the equipment requirements have been identified as main problems for the integration of these technologies to FCC units. CLC could be another method for CO₂ capture from the regenerator of FCC units. The CLC process, where metal oxides supply oxygen instead of air for combustion [16], has been suggested as an alternative process to decrease

CO₂ capture cost [17]. In CLC, the air and fuel are not mixed [18] so it does not need a separation process [16, 19], unlike PCC [5-8, 20], or OCC which has an air separation unit [11, 13, 21].

In this study, the applicability of CLC for FCC has been assessed as an innovative approach for the CO₂ capture from the regenerator of FCC units. Furthermore, the CLC-FCC concept aims to develop the next generation of FCC units to optimise CO₂ capture rather than the retrofitting of existing units. To show the potential applicability of the CLC-FCC concept, three key aspects of the process have been investigated; (i) the modification of commercial FCC catalyst with reduced oxygen carriers, (ii) the ineffectiveness of reduced oxygen carriers on the cracking reactions, (iii) the oxidation (or combustion) of coke with oxidised oxygen carriers at temperatures of *ca.* 750 °C, the maximum currently used for regeneration [22].

2 The proposed CLC-FCC concept

CLC technology has been employed for the combustion of various fuels such as natural gas, syngas, coal, biomass, petroleum coke, and hydrocarbon-based liquid fuels, with a wide range of oxygen carriers including Fe₂O₃, CuO, NiO, Mn₂O₃, and Co₃O₄, [16, 23-25], using different size lab and pilot scale reactors [19, 24, 26-28]. In addition to producing CO₂ rich flue gas, CLC serves to decrease NO_x emissions as no direct interaction between the air and fuel occurs. Furthermore, compared to OCC and PCC, CLC does not require capital-intensive air and CO₂ separation units.

In principle, commercial FCC catalysts can be modified with an oxygen carrier. Since deactivated FCC catalysts typically only contain 1-2 wt. % coke, relatively small amounts of oxygen carriers would be required for the combustion (or oxidation) of the coke. Furthermore, there is the possibility of incorporating oxygen carriers into the binders and fillers used in FCC catalyst formulations.

The proposed CLC-FCC concept is presented in Figure 1. The oxygen carrier in the fresh catalyst would be in a reduced state (designated Me_nO_{m-1}/Cat) as it enters the FCC reactor. The spent or deactivated catalyst with deposited coke assigned as $Coke/Me_nO_{m-1}/Cat$ is then transferred to the regenerator. The Me_nO_{m-1}/Cat catalyst would also be circulated to the air reactor via another fluidised bed, where the reduced state is oxidised designated as Me_nO_m/Cat . By the mixing of $Coke/Me_nO_{m-1}/Cat$ and Me_nO_m/Cat in the regenerator, the coke would be oxidised to CO₂ + H₂O while the oxidised oxygen carrier reduced to Me_nO_{m-1}/Cat . The concentrated CO₂ is then captured from the regenerator. The Me_nO_{m-1}/Cat is then circulated back to both the FCC reactor and the air reactor. Given that the cracking and metal oxidation reactions are fast in relation to the oxidised metal coke combustion, the average coke content of the catalyst in the regenerator would be low meaning that little CO₂ will be lost through combustion in the air reactor where the residence time will be short. The reactions for

CLC of carbon above indicate that all heat is generated in the air reactor and this needs to balance the heat required for the combustion and cracking reactions. The net CLC reaction and the reactions in the regenerator and air reactor for CuO, are given in reactions R1-R3.

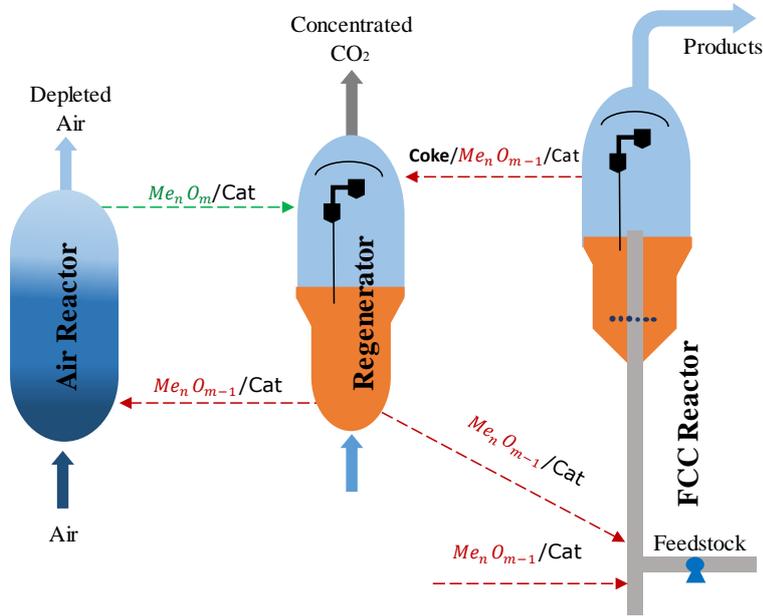
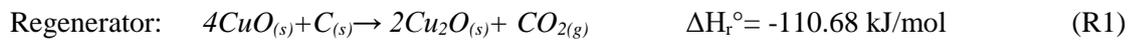


Figure 1. Schematic diagram of the proposed novel CLC-FCC process.



ΔH_r° and ΔH_o° are the standard heats of reaction for the reduction and oxidation at 298K and 1 atm.

Coke combustion with oxygen carriers may occur by two different mechanisms. Firstly, gas phase oxygen released from the oxygen carriers thanks to their chemical looping with oxygen uncoupling (CLOU) properties, and secondly via solid-solid interactions between coke and oxygen carrier. NO_x emission is another issue in conventional FCC that demands a control strategy [29], and CLC may be advantageous in that NO_x emissions would be lower than for normal combustion [30, 31].

Additionally, the concept will not comprise the need to control SO_x emissions and varying the zeolite composition to optimise product yields for different feedstock, for example adding ZSM-5 to increase alkene yields [30, 32]. Clearly, the concept is aimed at developing the next generation of FCC units to optimise CO₂ capture.

3 Materials and methods

3.1 Modification of ECat with reduced oxygen carriers

3.1.1 Preparation of reduced oxygen carriers

The reduction procedure for the oxidised oxygen carriers, CuO (98.0 %), Co₃O₄ (99.0 %), and Mn₂O₃ (99.0 %) supplied by Sigma Aldrich is as follows: Firstly, 20 g were placed into a porcelain crucible within the central zone of a horizontal tubular furnace. The furnace temperature was then increased from room temperature to 900 °C, at a heating rate of 20 °C/min, and kept at this temperature for 3 h under an N₂ flow of 2 L/min. As demonstrated by reactions R4 - R6 [19], at this temperature, the oxidised oxygen carriers; CuO, Co₃O₄, and Mn₂O₃ are reduced to Cu₂O, CoO, and Mn₃O₄, respectively. The furnace was then switched off and allowed to cool to room temperature.



3.1.2 Mechanical mixing of the reduced oxygen carriers with ECat

For modifying the FCC catalyst, a refinery equilibrium catalyst (ECat), a mechanical mixing method was employed. The required amount of oxygen carrier; CuO, Co₃O₄, and Mn₂O₃, was determined by considering the amount of coke on the FCC catalyst [22, 33-38] and the molecular weightz of the reduced and oxidised oxygen carriers. The reduced oxygen carriers, 0.23 g of Cu, 0.51 g of Cu₂O, 0.81 g of CoO, and 1.64 g of Mn₃O₄, were then mechanically mixed with 4.0 g of ECat using an angle vertical rotator (PTR-35, Grant-bio) for 10 min, and designated as M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat and M-Mn₃O₄/ECat.

3.2 Catalytic cracking activity of reduced oxygen carrier mixed ECat

3.2.1 Catalytic cracking activity tests

The catalytic cracking activity of reduced oxygen carriers modified ECat catalysts were investigated in a microactivity test (MAT) unit described in ASTM D3907 [39], a standard method for testing of FCC catalysts. The MAT experimental set-up, illustrated in Figure 2, consists of a Pyrex glass tubular reactor with an internal diameter of 1.9 cm and length of 27 cm, a temperature controlled tubular furnace, a syringe pump, a liquid product receiver and a gas bag. The reactor is located in a cylindrical furnace whose temperature measured by a vertically located thermocouple in contact with the glass wool.

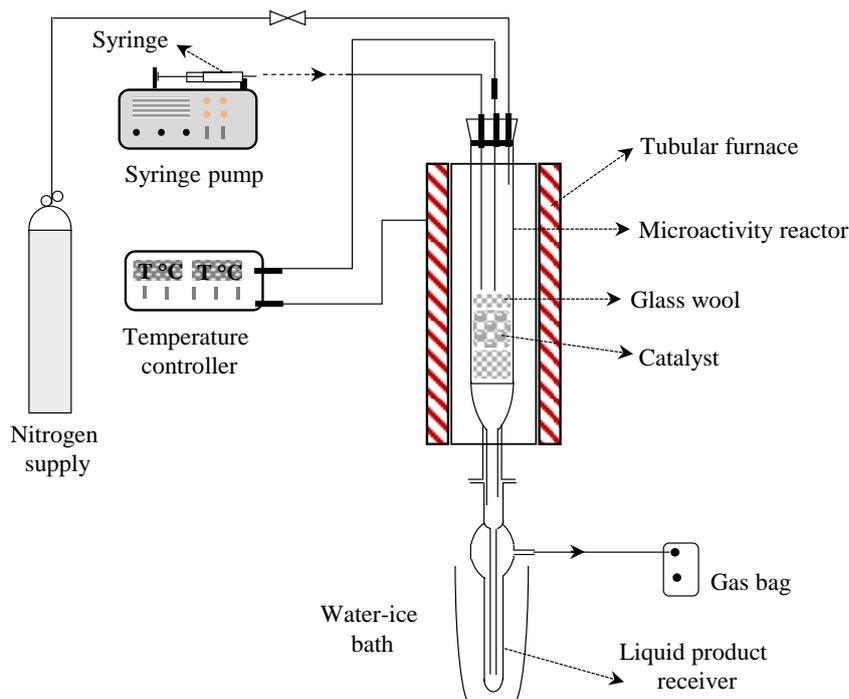


Figure 2. The experimental set-up of the MAT unit [39].

n-hexadecane was selected as a model cracking feed, and the experimental conditions reported in the ASTM D3907 standard were modified accordingly. Thermal cracking without catalyst and with the ECat were first carried out. The reduced oxygen carriers mixed ECat; M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat and M-Mn₃O₄/ECat, were then tested with the prepared catalysts placed between two pieces of glass wool in the MAT reactor located in the tubular furnace. The reactor temperature was then increased to 482 °C (± 5 °C) with a heating rate of 20 °C/min, under an N₂ flow of 20 ml/min. Once the reaction temperature had been attained, the system was purged with N₂ for 30 min. The feed, n-hexadecane, was then introduced to the MAT reactor at a rate of 1.38 ml/min for 75 s. During this injection period, the N₂ flow was switched off and the feed injection temperature was controlled by a vertically located thermocouple in contact with the glass wool bed. After injection, the reactor and product recovery system was purged with an N₂ flow of 20 ml/min for 15 min. The liquid products were condensed in the liquid product receiver using a water-ice bath, and the cracked gases were collected in a 1 litre gas bag. To reduce experimental error, the tests were repeated three times, and the yields are presented with error bars representing one standard deviation.

The liquid products obtained were analysed using a Clarus 580 GC (Perkin Elmer Elite-1 phase 60 m x 0.25 mm x 0.25 μ m capillary column) fitted with an FID detector. An aliquot, 1 μ l, of the liquid sample (diluted in dichloromethane) was injected at 250 °C with helium as the carrier gas. The gaseous products were immediately analysed after collection in the gas bag using a Clarus 580 GC

fitted with an FID and TCD detectors for the hydrocarbon and non-hydrocarbon gases respectively, operating at 200 °C. 5 ml of gas samples were injected (split ratio 10:1) at 250 °C with separation performed on an alumina plot fused silica 30 m x 0.32 mm x 10 µm column, with helium as the carrier gas. The oven temperature was programmed from 60 °C (13 min hold) to 160 °C (10 min hold) at 10 °C/min. The carbon (coke) contents of the used catalysts were determined by elemental analysis using a Leco CHN628 analyser.

3.2.2. Data evaluation

Conversions of n-hexadecane (Equation 1 and 2) to coke, liquid, and gas (Equation 3, 4 and 5) and product selectivities (Equation 6) to C₁₋₂ (dry gas), C₃₋₄ (LPG), C₅₋₁₅ (gasoline), C₁₆₊ (higher hydrocarbons) were determined.

$$\text{Conversion (overall) wt. \%} = \frac{W_{C_{16,0}} - W_{C_{16,f}}}{W_{C_{16,0}}} * 100 \quad (\text{E1})$$

$$\text{Conversion (excluding CLC) wt. \%} = \frac{W_{C_{16,0}} - (W_{C_{16,f}} + W_{CO_2})}{W_{C_{16,0}}} * 100 \quad (\text{E2})$$

$W_{C_{16,0}}$: The weight of n-hexadecane feed (g), $W_{C_{16,f}}$: The weight of uncracked n-hexadecane in the products (g), W_{CO_2} : Total weight of carbon in carbon dioxide in the products (g).

$$\text{Gas yield} = \frac{W_g}{W_{C_{16,0}}} * 100 \quad (\text{E3})$$

$$\text{Coke yield} = \frac{W_C}{W_{C_{16,0}}} * 100 \quad (\text{E4})$$

$$\text{Liquid yield} = \frac{(W_{C_{16,0}} - W_{C_{16,f}} - W_g - W_C)}{W_{C_{16,0}}} * 100 \quad (\text{E5})$$

$W_{C_{16,0}}$: The weight of n-hexadecane feed (g), $W_{C_{16,f}}$: The weight of uncracked n-hexadecane in the products (g), W_g : Total weight of gas products (g), W_C : Total weight of coke (g).

$$\text{Selectivity of i (wt. \%)} = \frac{W_i}{\sum W_{\text{products}}} * 100 \quad (\text{E6})$$

W_i : The weight of i product (C₁₋₂ (dry gas), C₃₋₄ (LPG), C₅₋₁₅ (gasoline), C₁₆₊ (higher hydrocarbons) and coke), g. $\sum W_{\text{products}}$: Total weight of the products C₁₋₂, C₃₋₄, C₅₋₁₅, C₁₆₊, and Coke, g.

3.3 CLC of model coke with the oxygen carriers

To investigate the combustion of coke deposited on FCC catalyst with the oxygen carriers, CLC tests were carried out using a Discovery TGA (TA instruments) which can operate with fast heating rates. In the TGA experiments, because of the low carbon contents (*ca.* 1%) of the used ECat and the weight limitation of TGA pans, a low volatile semi-anthracite Welsh coal having a similar chemical

composition to FCC coke (Table 2) was selected as a model FCC coke for the CLC tests. Regarding the oxygen carriers, commercially available CuO, Co₃O₄, and Mn₂O₃ were used.

3.3.1. Characterisation of model coke (low volatile semi-anthracite)

The coal was characterised by proximate and ultimate analyses. The coal was first dried at 105 °C for 24 h and then to collect the samples in 53-75 µm, ground and sieved. The proximate analyses were performed in the Discovery TGA (TA instruments) using the following procedure. Approximately 30 mg of model coke was loaded in a platinum pan 4 mm deep and 10 mm in diameter. It was then heated from ambient temperature to 110 °C with a heating rate of 50 °C/min and kept at this temperature for about 10 min under N₂ with a flow rate of 100 ml/min to remove moisture. It was then heated from this temperature to 1000 °C with a heating rate of 500 °C/min under same N₂ flow rate and kept about 20 min to remove volatile matter. Finally, to combust the fixed carbon, N₂ flow was replaced by air with a flow rate of 100 ml/min at the same temperature for 15 min. The ultimate analysis of coal (CHN and S) was determined using Leco CHN 628 and 628 S instruments.

3.3.2. CLC tests with the model coke

The model coke was physically mixed with the oxygen carriers, CuO, Co₃O₄, and Mn₂O₃, at three different oxygen excess numbers including R = 0.5, 1.0, and 2.0. For example, each gram of model coke stoichiometrically required 26.32 g of CuO, 34.50 g of Co₃O₄, and 67.85 g of Mn₂O₃ for the combustion under the oxygen excess number of R = 1.0. After mixing of oxygen carrier and model coke, the mixture was loaded in the platinum pan. The mixture was then heated from ambient temperature to 110 °C with a heating rate of 50 °C/min and kept at this temperature for 5 min to remove all the moisture. It was then rapidly heated from this temperature to combustion temperature, 750-900 °C, with a heating rate of 500 °C/min under a N₂ flow rate of 100 ml/min and held at the final temperature isothermally, under same N₂ flow rate, until combustion either was completed or had reached a limiting value. Finally, to burn off any remaining fixed carbon, the N₂ flow was replaced by air at the same temperature for 15 min. To reduce systematic errors, all TGA tests were repeated three times.

3.3.3. Data evaluation for the CLC tests

The combustion percentage of the fixed carbon in the hard coke and fractional reduction were calculated using the Equations 7 and 8 respectively [40-42].

$$\text{Combustion wt. \%} = \frac{M_{\text{HC},f}}{M_{\text{HC},0}} * 100 \quad (\text{E7})$$

M_{HC,f}: Actual mass loss of hard coke from TGA, M_{HC,0}: The theoretical hard coke mass was determined from the carbon content.

$$X_R = \frac{M_0 - M_t}{M_0 - M_f} \quad (E8)$$

X_R : The fractional reduction of coke + oxygen carrier mixture, M_0 : The mass of model coke + oxygen carrier mixture before combustion, (g), M_f : The mass of completely combusted of model coke + oxygen carrier mixture (reduced oxygen carrier + ash), (g), M_t : Instantaneous mass of model coke + oxygen carrier mixture, g.

4 Results and discussion

4.1 Catalytic cracking activity of the reduced oxygen carriers mixed with ECat

4.1.1 Reduction of the oxygen carriers

The XRD patterns of the oxygen carriers confirmed that reduction from CuO to Cu₂O, from Co₃O₄ to CoO, and from Mn₂O₃ to Mn₃O₄ had occurred as shown in Figure 3. The peaks at 29.5°, 36.4°, 42.3°, 52.5°, 61.3°, 73.5°, and 77.2° in pattern-c are the characteristic peaks for Cu₂O (JCPDS no:01-075-1531). The peaks at 36.5°, 42.3°, 61.5°, 73.7°, and 77.5° in pattern-b can be indexed to the phase of CoO crystals (JCPDS no: 00-043-1004). For pattern-a, the peaks at 18.1°, 29.0°, 31.1°, 32.3°, 36.1°, 38.0°, 44.4°, 49.7°, 50.7°, 54.0°, 56.0°, 58.5°, 59.9°, 64.7°, 69.8°, 74.1°, and 76.5° demonstrate the successful reduction from Mn₂O₃ to Mn₃O₄ (JCPDS no: 01-080-0382).

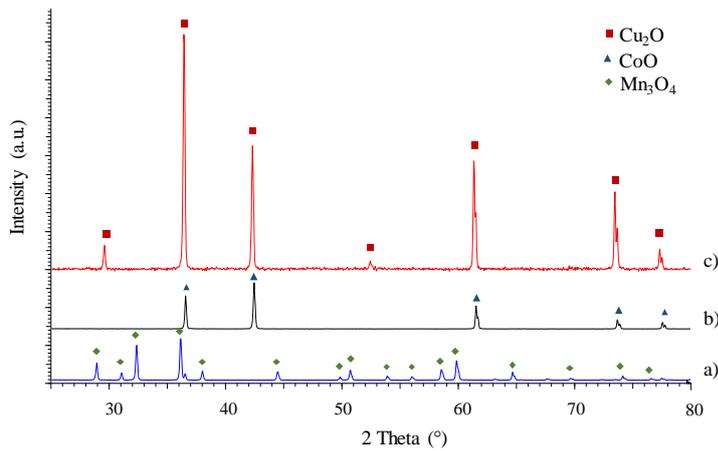


Figure 3. XRD patterns of the prepared reduced oxygen carriers; a) Mn₃O₄, b) CoO, c) Cu₂O.

4.1.2 Characterization of the used reduced oxygen carriers mixed with ECat

XRD analysis of the used catalysts was investigated to identify any crystalline deformation of the reduced oxygen carriers mixed with the ECat. The characteristic ECat peaks (marked with black stars) remain after cracking for samples M-Mn₃O₄/ECat, M-CoO/ECat, and M-Cu₂O/ECat as seen in Figure

4. Whilst the characteristic peaks for CoO remain for the used M-CoO/ECat (Figure 4-c), both M-Mn₃O₄/ECat and M-Cu₂O/ECat demonstrate a group of peaks assigned to MnO and Cu, (Figures 4-b and -d, respectively). The further reduction that occurred was semi-quantified using the intensities of XRD peaks and found to be approximately 11 % of the Cu and 5 % of the MnO in the respective used catalysts. This further reduction observed after cracking may be attributed to the CLC of the hydrocarbon feed (or cracked products) with the residual oxidised oxygen carriers. While carbon can combust with CuO at 482 °C, it needs much a higher temperature, nearly 624 °C, for its combustion with Cu₂O [43]. Additionally, the intensity of the reduced MnO and Cu peaks are much lower compared to initial reduced forms; Mn₃O₄ and Cu₂O. This reduction can clearly be eliminated with the use of completely reduced oxygen carriers.

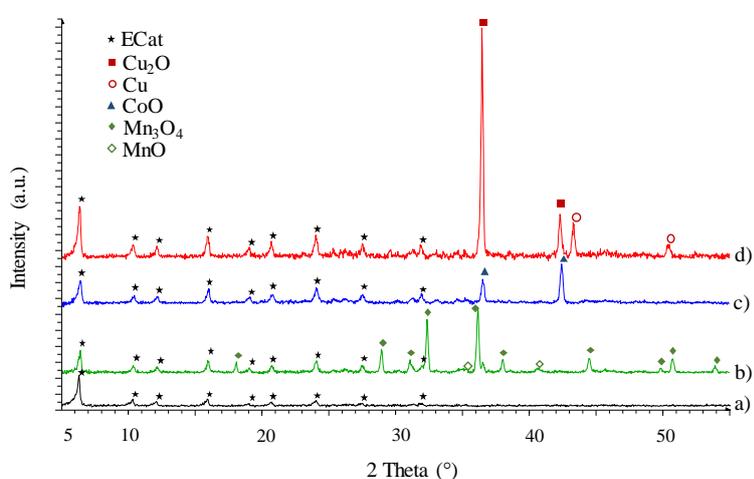


Figure 4. XRD patterns of a) fresh ECat and b) used M-Mn₃O₄/ECat c) used M-CoO/ECat d) used M-Cu₂O/ECat.

Table 1. Measured carbon and hydrogen contents and their normalised contents for the used ECat, M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat, and M-Mn₃O₄/ECat.

Catalyst	Coke on catalyst (wt. %)		Coke composition* (wt. %)		H/C
	Carbon (±0.00-0.09)	Hydrogen (±0.00-0.03)	Carbon (±1.0-3.0)	Hydrogen (±1.0-3.0)	
ECat	0.45	0.03	93.6	6.4	0.80
M-Cu/ECat	0.43	0.01	97.5	2.5	0.28
M-Cu ₂ O/ECat	0.39	0.03	93.2	6.8	0.92
M-CoO/ECat	0.42	0.02	95.0	5.0	0.57
M-Mn ₃ O ₄ /ECat	0.73	0.06	92.2	7.8	0.98

* Normalized coke composition was calculated by (weight of carbon / weight of coke)*100

The amount of coke deposited on the catalysts, ECat, M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat, and M-Mn₃O₄/ECat, during cracking of n-hexadecane was less than 1.0 wt. % (Table 1). Further, the amount of coke on the ECat did not significantly change after the reduced oxygen carrier was mixed

with the ECat The atomic H/C ratios 0.28-0.98, are comparable to those reported in the literature e.g. 0.46-1.74 [34]. However, the hydrogen contents were slightly higher than the literature values [34] which may be attributed to residual on the catalysts.

4.1.3. The cracking reaction of *n*-hexadecane over the reduced oxygen carriers mixed ECat

Figure 5 demonstrates that mixing of metallic Cu with the ECat had a detrimental effect with the conversion decreasing from 40 to 30 wt. %. Such a detrimental effect of Cu on the conversion of palm oil cracking has also been observed by Siregar and Amin [44], who attributed this to a decrease in the Brönsted acidity. However, in this study the Brönsted acidity should not be adversely affected by the mechanically mixed reduced oxygen carriers. The decrease in the conversion may, therefore, be explained by the negative interaction between *n*-hexadecane and metallic Cu. On the other hand, conversion was not adversely affected by Cu₂O (38 wt. %), CoO (43 wt. %), and Mn₃O₄ (45 wt. %).

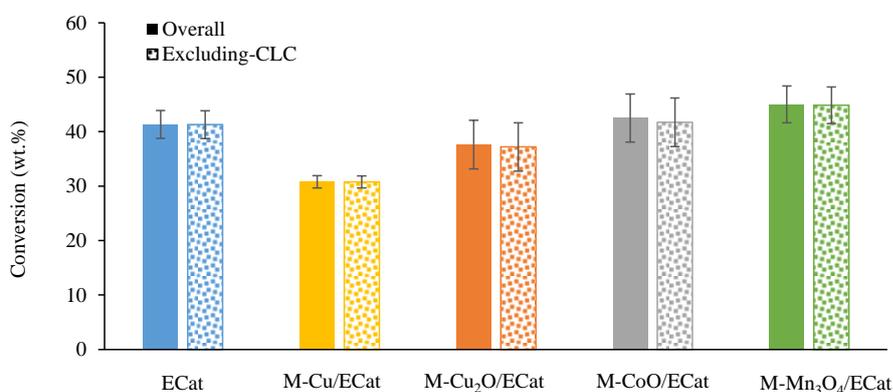


Figure 5. The conversions (overall and excluding CLC) of *n*-hexadecane over ECat and the reduced oxygen carrier mixed ECat samples; M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat, and M-Mn₃O₄/ECat (the error bars represents the standard deviation calculated by triple experiments).

The coke, gas, and liquid yields are presented in Figure 6. Cu, Cu₂O, and CoO mixed ECat are shown not to have a significant effect on the coke yield obtained, approximately 1.4 wt. %, whereas the coke yield increased from 1.5 to 2.7 wt. % for Mn₃O₄. While both gas and liquid yields decreased to *ca.* 17 wt. % and 13 wt. %, respectively, for Cu, they were not affected significantly for Cu₂O, CoO and Mn₃O₄, being approximately 21 wt. % and 18 wt. %, respectively (Figure 6).

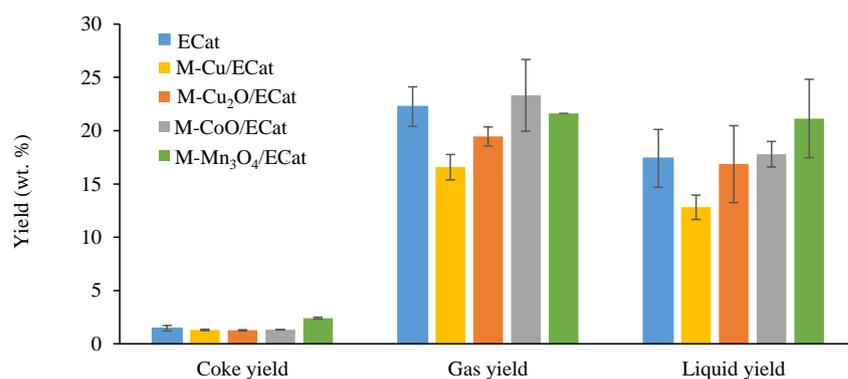


Figure 6. Coke, gas, and liquid yields from the cracking of n-hexadecane over ECat and the reduced oxygen carrier mixed ECat samples; M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat, and M-Mn₃O₄/ECat.

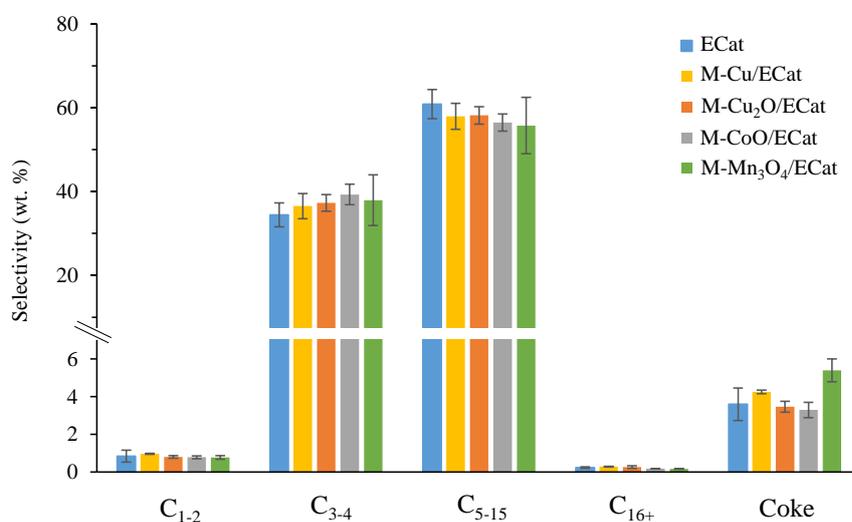


Figure 7. The product selectivities for C₁₋₂ (light gases), C₃₋₄ (LPG), C₅₋₁₅ (gasoline), C₁₆₊ (higher hydrocarbons) and coke from the cracking of n-hexadecane over commercial ECat and reduced oxygen carrier mixed ECat samples; M-Cu/ECat, M-Cu₂O/ECat, M-CoO/ECat, and M-Mn₃O₄/ECat.

The product selectivities for the un-modified ECat and reduced oxygen carrier mixed ECat samples are presented in Figure 7. The reduced oxygen carriers have a negligible effect on the selectivities for C₁₋₂, C₃₋₄, C₅₋₁₅, and C₁₆₊, as desired for CLC-FCC [45]. Additionally, although the mixing of Cu, Cu₂O and CoO with the ECat had an insignificant effect on the coke selectivity which was *ca.* 3.8 wt. %, Mn₃O₄ slightly increased this from *ca.* 3.6 to 5.4 wt. %. This may be attributable to the increase in catalyst volume with the mixing of Mn₃O₄. Thus, overall, mixing of Cu₂O, CoO, and Mn₃O₄ with ECat has a negligible effect on the cracking reactions in terms of both product yields and selectivities.

4.2. CLC tests of the model coke with the oxygen carriers

4.2.1. Oxygen carriers and model coke behaviour under TGA experiment conditions

The proximate and ultimate analyses presented in Table 2 indicate that the semi-anthracite has a similar elemental composition to FCC coke (Table 2), and, on this basis, was selected for the CLC experiments as a model coke.

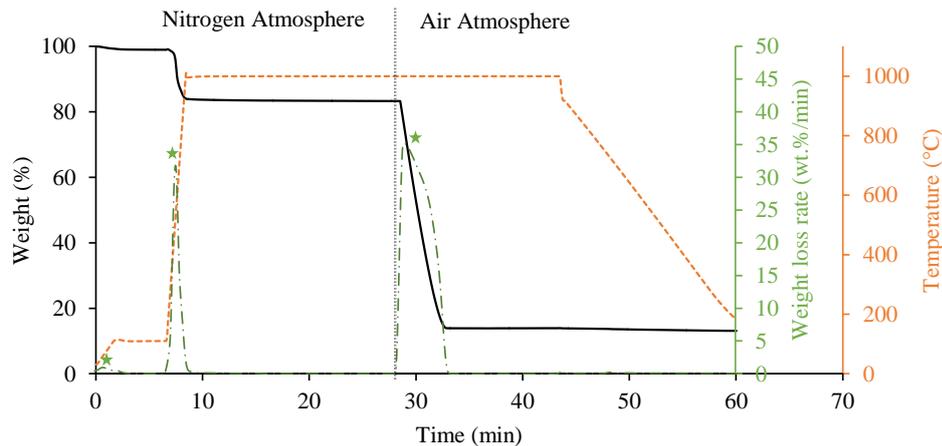


Figure 8. TGA profile of the model coke under nitrogen and then air at at 1000 °C.

The TGA results of the oxidised oxygen carriers (not shown) demonstrated that the weight loss percentages for the reductions from CuO to Cu₂O, Co₃O₄ to CoO and M₂O₃ to Mn₃O₄ are *ca.* 10.1, 6.4, and 3.6 wt. %, respectively, close to their theoretical values. The results proved that the oxygen carriers can release their oxygen due to their CLOU properties as it has been demonstrated in the literature [19, 40, 43, 46]. The oxygen released from oxygen carriers can be therefore used to combust the coke on the FCC catalysts if effective mixing with the model coke exists.

Table 2. Ultimate and proximate analysis of the semi anthracite model coke and normalized elemental analyses of the model and FCC cokes.

Ultimate analysis ^a (wt. %)					Proximate analysis ^c (wt. %)			
C	H	N	S	O ^b	TM ^d	VM	FC	Ash
86.3	4.3	1.5	2.2	5.7	0.5	16.2	70.3	13.5
Normalized element analysis (wt. %) of model coke and FCC cokes								
Coke type	C %	H %	N %	S %	References			
Model coke	91.6	4.6	1.6	2.3	-			
FCC coke-1	91.2	4.2	2.5	1.9	[34]			
FCC coke-2	93.0	2.9	3.8	0.4	[34]			
FCC coke-3	93.0	2.6	3.0	0.1	[34]			

TM: Total Moisture, VM: Volatile matter, FC: Fixed carbon. ^a Dry basis, ^b Determined by difference, ^c On dry basis except moisture which is as received basis, ^d As received basis.

4.2.2. CLC tests for the model coke with CuO

The effects of temperature and oxygen excess number (according to reaction R7) on the combustion of model coke with CuO are presented in Figure 9. It is possible to reach higher than 90 wt. % combustion with the minimum stoichiometrical requirement (R= 1.0) for CuO over the range 750 to 900 °C. Thus, increasing the oxygen excess number from 1.0 to 2.0 had an insignificant effect. Further, as expected, decreasing the oxygen carrier below the stoichiometric ratio decreased the extent of combustion (for R=0.5, 46, 31, 40 and 41 wt. % at 900, 850, 800, and 750 °C, respectively, Figure 9).

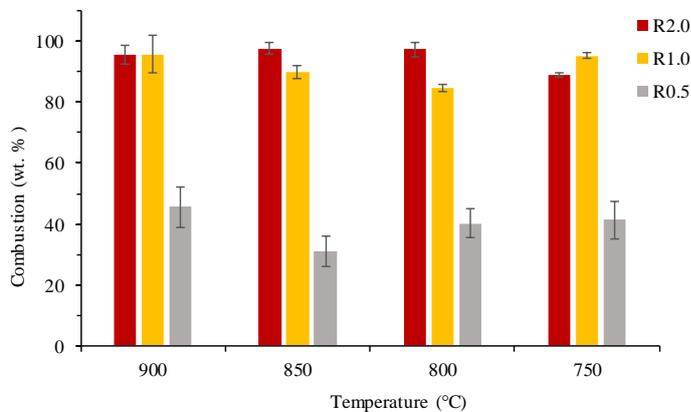
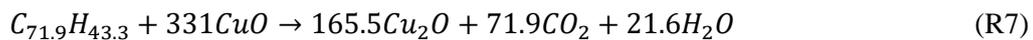


Figure 9. Combustion (wt. %) of model coke with CuO in various oxygen excess numbers (R = 0.5, 1.0, and 2.0) at different isothermal temperatures (750-900 °C).

The fractional reductions of the model coke with CuO for different oxygen excess numbers are presented in Figure 10 where WC refers to the model coke, Cu indicates CuO and R0.5, R1.0 and R2.0 refers to the oxygen excess numbers. As demonstrated in Figure 10, the fractional reduction tends to decrease with the isothermal combustion temperature as reported by Siriwardane et al. [42] for the combustion of solid fuels with oxygen carriers. For example, for the fractional reduction to reach above 0.8 at 900, 850, 800, and 750 °C, times of 1, 3, 9, and 45 min, respectively, were required (R = 1.0). These differences, especially below 800 °C, can possibly be attributed to the partial pressure of oxygen released from CuO at the isothermal temperatures being 15 times higher at 900 °C (15×10^{-3}) than that at 800 °C (1.0×10^{-3}) [19, 43].

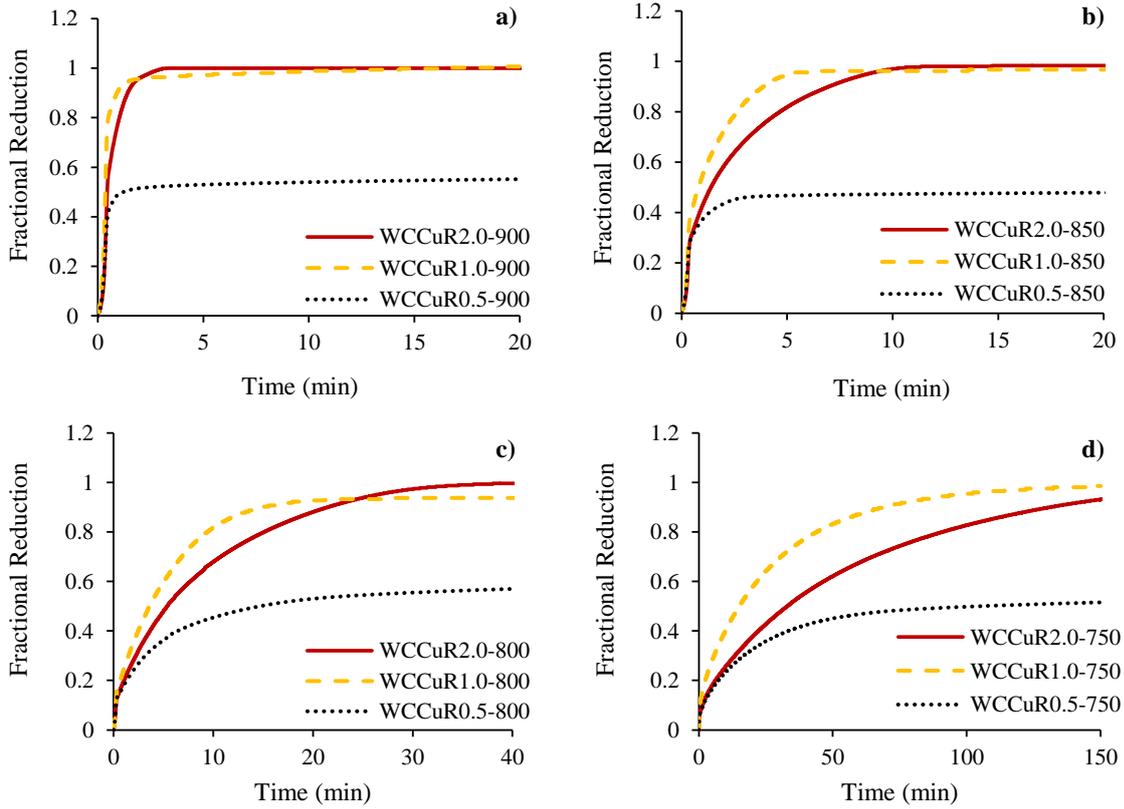
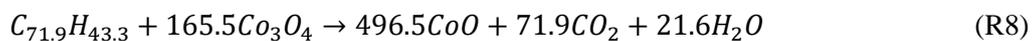


Figure 10. Fractional reduction of the model coke with CuO for various oxygen excess numbers ($R = 0.5, 1.0, \text{ and } 2.0$) at different temperatures a) 900 °C, b) 850 °C, c) 800 °C, d) 750 °C.

Clearly, the oxygen excess number clearly needs to be equal or higher than the stoichiometric level to achieve a fractional reduction of 1.0 and complete combustion [47], which was achieved here with stoichiometric amount of CuO ($R \geq 1.0$) and allowing sufficient time (Figure 10). However, using excessive oxygen carrier sometimes negatively affects the fractional reduction. Figure 10 indicates that longer times were required to achieve high fractional reductions once the oxygen excess number was 2.0 (red-continuous line). This may be due to increasing inhomogeneity in the mixtures with the model coke which will be a negatively impact on solid-solid interactions. As expected, fractional reductions fell below the stoichiometrical requirement ($R = 0.5$). The high fractional reductions for CuO with the model coke when $R = 1.0$ is consistent with other reports for the combustion of coal with oxygen carriers [43, 48, 49].

4.2.3. CLC tests of the model coke with Co_3O_4

The results are presented in Figure 11, the combustion reaction of the model coke with Co_3O_4 being represented in reaction R8.



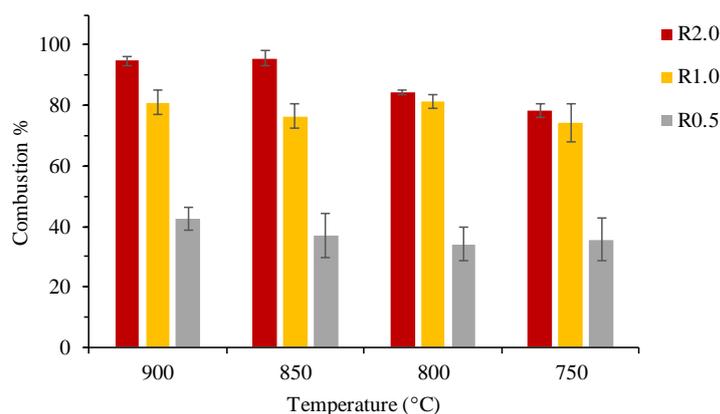


Figure 11. Combustion (wt. %) of the model coke with Co_3O_4 for various oxygen excess numbers ($R = 0.5, 1.0, \text{ and } 2.0$) at different isothermal temperatures (750-900 °C).

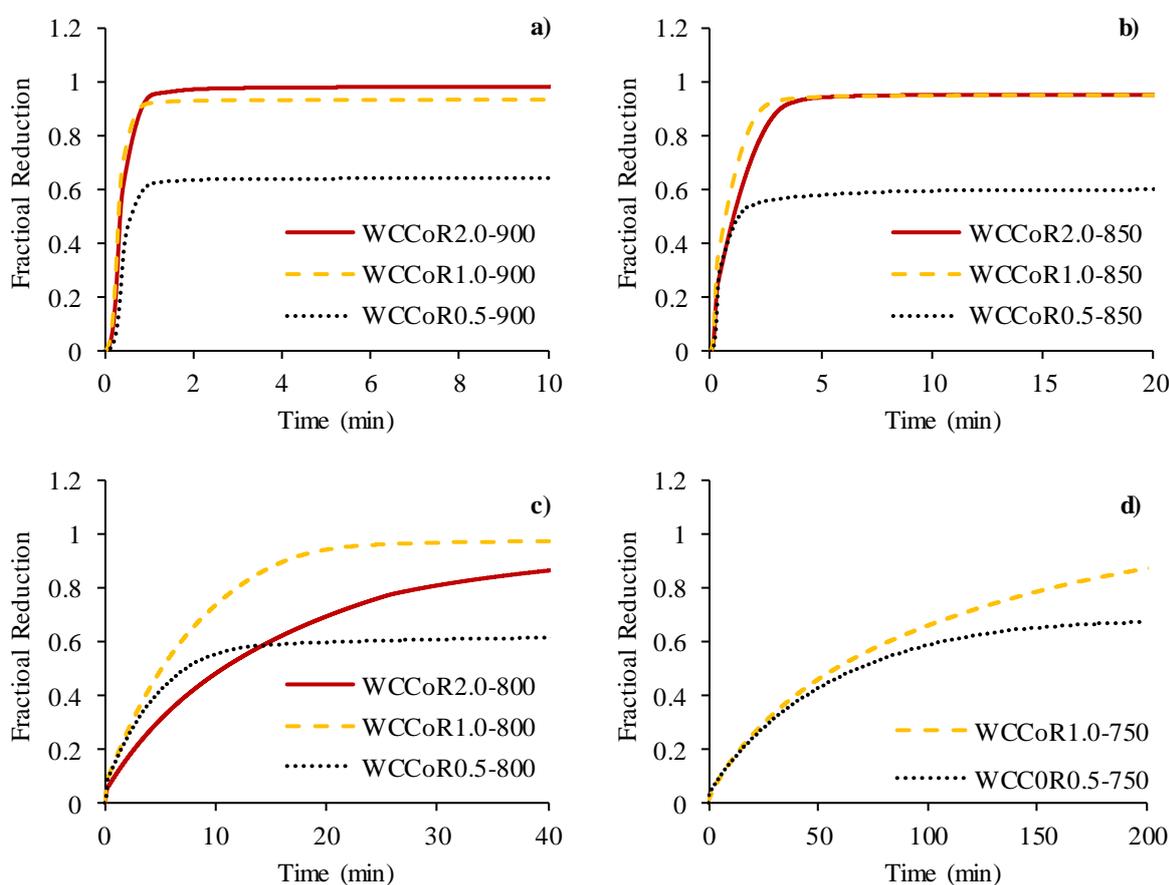


Figure 12. Fractional reduction of the model coke with Co_3O_4 for various oxygen excess numbers ($R = 0.5, 1.0, \text{ and } 2.0$) at different temperatures a) 900 °C, b) 850 °C, c) 800 °C, d) 750 °C, °C.

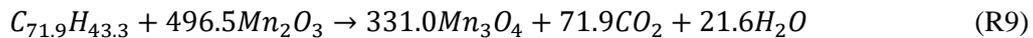
Figure 11 shows that the extent combustion increased with temperature and was over 80 wt. % using the stoichiometrically required amount of Co_3O_4 . However, as also observed for CuO , using higher than the stoichiometrically required amount of Co_3O_4 , slightly increased the extent of combustion at

all temperatures. However, the extent of combustion of model coke with CuO was higher than that with Co₃O₄. For example, the combustion % was as approximately 90 wt. % for CuO compared to 80 wt. % for Co₃O₄ at 850 °C, as demonstrated in Figures 10 and 11.

It is possible to reach high fractional reductions at high temperatures in seconds. However, for a fractional reduction of 0.9, 20 min is required 800 °C (R = 1.0 and 2.0). However, once the temperature decreased to 750 °C, the fractional reduction was only 0.8 after 200 min due to the low partial pressure of O₂ over Co₃O₄, about $1.0 \cdot 10^{-3}$ at 750 °C which is 6 times lower than that at 800 °C and 49 times lower that at 850 °C [19].

4.3.4. CLC tests of the model coke with Mn₂O₃

The combustion of model coke was also investigated with Mn₂O₃, which can also show CLOU properties [19, 30, 50, 51] and the results are presented in Figure 13. Because of the relatively large amount of Mn₂O₃ requires, the experiments were investigated under 1.5 oxygen excess number instead of 2.0. The combustion of model coke with Mn₂O₃ is represented by the following reaction, R9.



It is possible to reach almost complete combustion using the required amount of Mn₂O₃ from 750 °C to 900 °C, shown in Figure 13. The extent of combustion was almost 100 wt. % once the oxygen excess number was 1. . When the oxygen excess number was kept at the stoichiometrical amount, 1.0, the extent of combustion was in the range 87-92 wt. %. Again, as expected, when insufficient oxygen carrier was present, such as for an oxygen excess number of 0.5, the extent of combustion was below 50 wt. % (Figure 13).

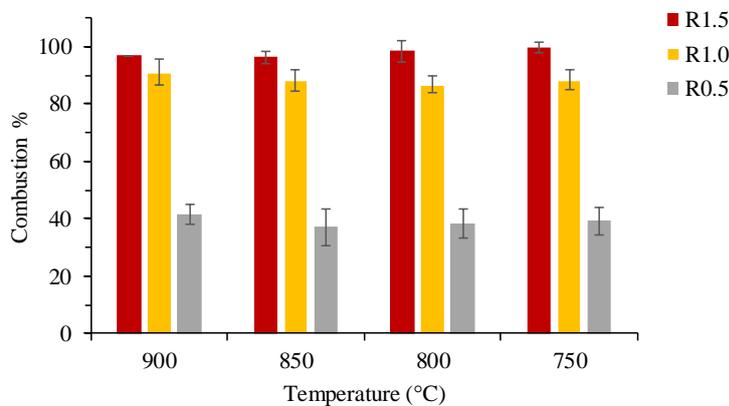


Figure 13. Combustion (wt. %) of the model coke with Mn₂O₃ with various oxygen excess numbers (R = 0.5, 1.0, and 1.5) at different i temperatures (750-900 °C).

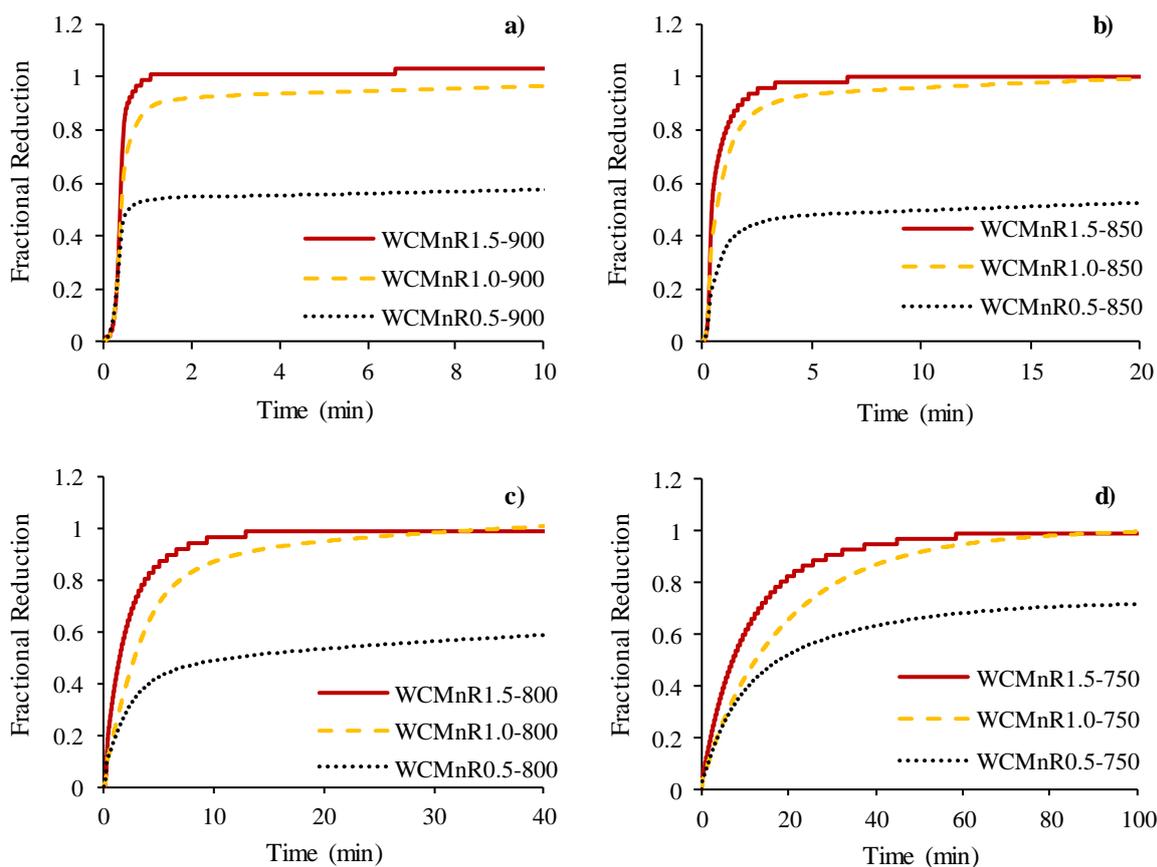


Figure 14. Fractional reduction of the model coke with Mn_2O_3 for various oxygen excess numbers ($R = 0.5, 1.0,$ and 1.5) at different temperatures a) $900\text{ }^\circ\text{C}$, b) $850\text{ }^\circ\text{C}$, c) $800\text{ }^\circ\text{C}$, d) $750\text{ }^\circ\text{C}$.

The fractional mass reductions of the model coke with Mn_2O_3 for the different oxygen excess numbers and temperatures are presented in Figure 14. The fractional reductions reach 1.0 in less than 40 min which is quite similar to the time for coke combustion in the conventional regenerator, approximately 30-60 min [52] at $750\text{ }^\circ\text{C}$ with the stoichiometrically required amount of oxygen carrier, $R = 1.0$, or more, $R = 1.5$. The increase in combustion temperature enhanced the fractional reduction as for CuO and Co_3O_4 . For instance, the fractional reduction reached 1.0 in seconds at $900\text{ }^\circ\text{C}$, in 5 min at $850\text{ }^\circ\text{C}$, and in 10 min at $800\text{ }^\circ\text{C}$ ($R = 1.0$ and 1.5).

In summart, CuO , Co_3O_4 , and Mn_2O_3 were tested as oxygen carriers for the combustion reached reasonable values, higher than 90 wt. %, in about 60 min using CuO and 40 min using Mn_2O_3 at $750\text{ }^\circ\text{C}$ for the oxygen excess number of 1.0. It will be important to further investigate the combustion of actual coke deposited on FCC catalyst with oxygen carriers in fluidised bed reactors will be used in continuous CLC-FCC operation.

5. Conclusions

In terms of cracking reactions, mixing of Cu with ECat was detrimental on the conversion of n-hexadecane. However, this was not the case for Cu₂O, CoO, and Mn₃O₄ in terms of the conversion, yields, and product selectivities. Although the mixing of CoO with ECat seems gives the closest conversions, in terms of gas, liquid and coke yields to the reference ECat, the other two reduced state oxygen carriers, Cu₂O and Mn₃O₄, were also demonstrated promising, with relatively small differences in conversion. As for the CLC tests of model coke with oxygen carriers; CuO, Co₃O₄ and Mn₂O₃, the TGA studies demonstrated that complete combustion is possible once the stoichiometrically required amounts of oxygen carriers and sufficient time have been provided. Additionally, it was achieved higher than 90 wt. % combustion of model coke with CuO and Mn₂O₃ at 750 °C for 40-60 min, almost similar conditions used in the conventional regenerator of FCC units. The findings have led us to conclude that CLC is a promising technology for the CO₂ capture from the regenerator of FCC unit, however, the investigations into this area are still in progress and the process operating conditions need to be improved.

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References

- [1] van Straelen J, Geuzebroek F, Goodchild N, Protopapas G, Mahony L. CO₂ capture for refineries, a practical approach. *International Journal of Greenhouse Gas Control* 2010;4(2):316-20.
- [2] John G, John B, Zhenlin C, Amit G, Dario G, Hans Holger R, et al. Sources of CO₂. In: Metz B, Davidson O, De Coninck H, Loos M, Meyer L, eds. IPCC special report on carbon dioxide capture and storage. Intergovernmental Panel on Climate Change. Working Group III; 2005:75-104.
- [3] van Straelen J, Geuzebroek F, Goodchild N, Protopapas G, Mahony L. CO₂ capture for refineries, a practical approach. *Energy Procedia* 2009;1(1):179-85.
- [4] EPA. Available and emerging technologies for reducing GHG emissions from petroleum refining. U.S. Environmental Protection Agency; 2010.
- [5] Elkamel A, Ba-Shammakh M, Douglas P, Croiset E. An optimization approach for integrating planning and CO₂ emission reduction in the petroleum refining industry. *Industrial & Engineering Chemistry Research* 2008;47(3):760-76.
- [6] Peng P, Zhuang Y. The evaluation and comparison of carbon dioxide capture technologies applied to FCC flue gas. *Advanced Materials Research*. 347. Trans Tech Publ; 2012:1479-82.
- [7] Digne R, Feugnet F, Gomez A. A technical and economical evaluation of CO₂ capture from fluidized catalytic cracking (FCC) flue gas. *Oil & Gas Science and Technology—Revue d'IFP Energies nouvelles* 2014;69(6):1081-9.
- [8] Miracca I, Butler D. CO₂ capture from a fluid catalytic cracking unit: Technical/Economical evaluation. In: Gerdes KF, editor *Carbon dioxide capture for storage in deep geologic formations*. CPL Press; 2015, p. 67-81.
- [9] de Mello LF, Pimenta RD, Moure GT, Pravia OR, Gearhart L, Milios PB, et al. A technical and economical evaluation of CO₂ capture from FCC units. *Energy Procedia* 2009;1(1):117-24.
- [10] Melien T, Brown-Roijen S. Economics. In: Lars E, editor *Carbon dioxide capture for storage in deep geologic formation-Results from the CO₂ capture project.*: CPL Press; 2009, p. 237-64.

- [11] de Mello LF, Gobbo R, Moure GT, Miracca I. Oxy-combustion technology development for fluid catalytic crackers (FCC)—large pilot scale demonstration. *Energy procedia* 2013;37:7815-24.
- [12] de Mello LF, Gobbo R, Moure GT, Miracca I. CO₂ capture from a fluid catalytic cracking unit. In: Gerdes KF, editor *Carbon dioxide capture for storage in deep geologic formations-Results from the CO₂ capture project*. CPL Press; 2015, p. 47-9.
- [13] de Mello LF, Gobbo R, Moure GT, Miracca I. FCC oxy-fuel demonstration at petrobras shale industrial business unit. In: Gerdes KF, editor *Carbon dioxide capture for storage in deep geologic formations-Results from the CO₂ capture project*. CPL Press; 2015, p. 51-65.
- [14] Crombie M, Imbus S, Miracca I. CO₂ capture project phase 3—Demonstration phase. *Energy Procedia* 2011;4:6104-8.
- [15] Metz B, Davidson O, De Coninck H, Loos M, Meyer L. IPCC special report on carbon dioxide capture and storage. Intergovernmental Panel on Climate Change. Working Group III; 2005.
- [16] Ksepko E, Siriwardane RV, Tian H, Simonyi T, Sciazko M. Effect of H₂S on chemical looping combustion of coal-derived synthesis gas over Fe–Mn oxides supported on sepiolite, ZrO₂, and Al₂O₃. *Energy & Fuels* 2012;26(4):2461-72.
- [17] Kerr HR. Capture and separation technology gaps and priority research needs. In: Thomas DC, Benson SM, editors. *Carbon dioxide capture for storage in deep geologic formations results from the CO₂ capture project*. Oxford, UK: Elsevier; 2005.
- [18] Pröll T, Kolbitsch P, Bolhár-Nordenkamp J, Hofbauer H. A novel dual circulating fluidized bed system for chemical looping processes. *AICHE journal* 2009;55(12):3255-66.
- [19] Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *International Journal of Greenhouse Gas Control* 2009;3(1):11-9.
- [20] Drage T, Arenillas A, Smith K, Snape C. Comparison of pre and postcombustion CO₂ adsorbent technologies. 8th International Conference on Greenhouse Gas Control Technologies. 2006:19-22.
- [21] de Mello LF, Moure GT, Pravia OR, Gearhart L, Milios PB. Oxy-combustion for CO₂ capture from fluid catalytic crackers (FCC) In: Lars E, editor *Carbon dioxide capture for storage in deep geologic formation-Results from the CO₂ capture project*. CPL Press; 2009, p. 31-42.
- [22] Corma A, Sauvanaud L, Occelli M. *Fluid Catalytic Cracking VII: Materials, Methods and Process Innovations*. Elsevier, BV, Amsterdam 2007.
- [23] Adánez J, de Diego LF, García-Labiano F, Gayán P, Abad A, Palacios J. Selection of oxygen carriers for chemical-looping combustion. *Energy & Fuels* 2004;18(2):371-7.
- [24] Adanez J, Abad A, Garcia-Labiano F, Gayan P, Luis F. Progress in chemical-looping combustion and reforming technologies. *Progress in Energy and Combustion Science* 2012;38(2):215-82.
- [25] Adánez J, García-Labiano F, Abad A, de Diego L, Gayán P, Dueso C. NiO-based oxygen carriers impregnated on Al₂O₃-based materials for chemical-looping combustion. *Carbon dioxide capture for storage in deep geological formations results from the CO₂ capture project* 2009;3.
- [26] Cho P, Mattisson T, Lyngfelt A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* 2004;83(9):1215-25.
- [27] Mattisson T, Lyngfelt A. Applications of chemical-looping combustion with capture of CO₂. Second Nordic Minisymposium on CO₂ Capture and Storage, Göteborg, Sweden 2001.
- [28] Tian H, Chaudhari K, Simonyi T, Poston J, Liu T, Sanders T, et al. Chemical-looping combustion of coal-derived synthesis gas over copper oxide oxygen carriers. *Energy & Fuels* 2008;22(6):3744-55.
- [29] Hicks JC, Drese JH, Fauth DJ, Gray ML, Qi G, Jones CW. Designing adsorbents for CO₂ capture from flue gas-hyperbranched aminosilicas capable of capturing CO₂ reversibly. *Journal of the American Chemical Society* 2008;130(10):2902-3.
- [30] Wang P, Means N, Shekhawat D, Berry D, Massoudi M. Chemical-looping combustion and gasification of coals and oxygen carrier development: a brief review. *Energies* 2015;8(10):10605-35.
- [31] Cao Y, Casenas B, Pan W-P. Investigation of chemical looping combustion by solid fuels. 2. Redox reaction kinetics and product characterization with coal, biomass, and solid waste as solid fuels and CuO as an oxygen carrier. *Energy & Fuels* 2006;20(5):1845-54.
- [32] Huang J, Zou J, Ho WW. Carbon dioxide capture using a CO₂-selective facilitated transport membrane. *Industrial & Engineering Chemistry Research* 2008;47(4):1261-7.
- [33] Shi J, Guan J, Guo D, Zhang J, France LJ, Wang L, et al. Nitrogen Chemistry and Coke Transformation of FCC Coked Catalyst during the Regeneration Process. *Sci Rep* 2016;6:27309.
- [34] Behera B, Gupta P, Ray SS. Structure and composition of hard coke deposited on industrial fluid catalytic cracking catalysts by solid state ¹³C nuclear magnetic resonance. *Applied Catalysis A: General* 2013;466:123-30.
- [35] Behera B, Ray SS. Structural changes of FCC catalyst from fresh to regeneration stages and associated coke in a FCC refining unit: A multinuclear solid state NMR approach. *Catalysis Today* 2009;141(1):195-204.

- [36] Voorhies Jr A. Carbon formation in catalytic cracking. *Industrial & Engineering Chemistry* 1945;37(4):318-22.
- [37] Qian K, Tomczak DC, Rakiewicz EF, Harding RH, Yaluris G, Cheng W-C, et al. Coke formation in the fluid catalytic cracking process by combined analytical techniques. *Energy & fuels* 1997;11(3):596-601.
- [38] Wear CC. 'Coke Selectivity Fundamentals. 75. Catalagram; 1987.
- [39] ASTM. Standard Test Method for Testing Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test. D3907-13. ASTM International; 2013.
- [40] Aghabarannejad M, Patience GS, Chaouki J. TGA and kinetic modelling of Co, Mn and Cu oxides for chemical looping gasification (CLG). *The Canadian Journal of Chemical Engineering* 2014;92(11):1903-10.
- [41] Tian H, Siriwardane R, Simonyi T, Poston J. Natural ores as oxygen carriers in chemical looping combustion. *Energy & Fuels* 2013;27(8):4108-18.
- [42] Siriwardane R, Tian H, Richards G, Simonyi T, Poston J. Chemical-looping combustion of coal with metal oxide oxygen carriers. *Energy & Fuels* 2009;23(8):3885-92.
- [43] Siriwardane R, Tian H, Miller D, Richards G, Simonyi T, Poston J. Evaluation of reaction mechanism of coal-metal oxide interactions in chemical-looping combustion. *Combustion and flame* 2010;157(11):2198-208.
- [44] Siregar TB, Amin N. Catalytic cracking of palm oil to gasoline over pretreated Cu-ZSM-5. *Jurnal Teknologi* 2006;44(1).
- [45] Rawlence DJ, Gosling K. FCC catalyst performance evaluation. *Applied Catalysis* 1988;43(2):213-37.
- [46] Adánez-Rubio I, Gayán P, García-Labiano F, Luis F, Adánez J, Abad A. Development of CuO-based oxygen-carrier materials suitable for chemical-looping with oxygen uncoupling (CLOU) process. *Energy Procedia* 2011;4:417-24.
- [47] Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* 2007;86(12-13):1947-58.
- [48] Wang B, Zhao H, Zheng Y, Liu Z, Zheng C. Chemical looping combustion of petroleum coke with CuFe₂O₄ as oxygen carrier. *Chemical Engineering & Technology* 2013;36(9):1488-95.
- [49] Piekiet NW, Egan GC, Sullivan KT, Zachariah MR. Evidence for the predominance of condensed phase reaction in chemical looping reactions between carbon and oxygen carriers. *The Journal of Physical Chemistry C* 2012;116(46):24496-502.
- [50] Rydén M, Lyngfelt A, Mattisson T. Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system. *Energy Procedia* 2011;4:341-8.
- [51] Zhang X, Banerjee S, Agarwal RK. Validation of chemical-looping with oxygen uncoupling (CLOU) using Cu-based oxygen carrier and comparative study of Cu, Mn and Co based oxygen carriers using ASPEN plus. *International Journal of Energy and Environment* 2015;6(3):247.
- [52] Arbel A, Huang Z, Rinard IH, Shinnar R, Sapre AV. Dynamic and control of fluidized catalytic crackers. 1. Modeling of the current generation of FCC's. *Industrial & engineering chemistry research* 1995;34(4):1228-43.