Oxy-cracking as an emerging technology for demineralization and conversion of petroleum coke

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Oxy-cracking as an emerging technology for demineralization and conversion of petroleum coke

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Abstract-Oxy-cracking technique, which is a combination of oxidation and cracking reactions, is developed as an alternative approach for petroleum coke (petcoke) demineralization and conversion into value-added product. The oxy-cracking takes place in basic aqueous media, at mild operation temperatures (170-230ºC) and pressures (500-600 psi). The reaction mechanism was investigated at several operating conditions on petcoke oxy-cracking, such as temperature, oxygen pressure, reaction time, particle size and mixing rate to optimize the conversion and selectivity of oxy-cracked products. The oxy-cracking technique successfully converted petcoke into valuable products, particularly humic acids analogs as confirmed by FTIR, with minimal emissions of CO_2. The metal contents in the obtained oxy-cracked products are significantly lower than that in the virgin petcoke. The oxidation behaviour of the oxy-cracked products was investigated using TGA. These results showed that the oxy-cracked petcoke is easier and faster to oxidize compared to the virgin petcoke, suggesting that the oxy-cracked petcoke could also be used as an alternative-clean fuel for power generation.

Keywords-petroleum coke, humic acids, metal recovery, fuel, CNT.

I. INTRODUCTION

Despite the variety of energy resources and the rise in technologies, the world still relies heavily on crude oil as the main energy source with a projected increased demand of 33% in 2035 [1]. Therefore, there is an increasing demand to upgrade and recover unconventional crude oil, like bitumen and heavy oil, to meet current and future global energy demands[2]. During bitumen and heavy oil upgrading and recovery processes, a large volume of carbon-rich solid waste by-product is produced known as petroleum coke, petcoke [3]. The global production of petcoke has reached about 150 million metric tons per annum and is expected to increase in the future due to the progressively increasing heavier nature of the crudes [4]. Currently, several thermal techniques have been proposed for generating energy from petcoke, such as gasification and combustion [5, 6]. However, the effectiveness of these conventional processes is limited due to sulfur and CO_2 emissions as well as high energy costs combined with low efficiency [7]. Herein, the oxy-cracking technique is developed as a new innovative technology for creating economic value from any residual feedstocks like petcoke, oil sands bitumen, residue streams and also mine reject asphaltenes by offering a new reaction pathway into an aqueous solution, thus converting them into valuable products such as humic acids, clean fuel, and metals recovery [8-11]. This novel approach has been investigated and validated extensively by our research group at the University of Calgary by employing a combination of oxidation and cracking (i.e., oxy-cracking) processes in an aqueous alkaline media at moderate temperatures (approx. 170 °C) and pressures (300-500 psi) [12]. Such a new reaction pathway can be achieved by changing the oxidation conditions, temperature and pressure, which alters the mechanism and results in different product distributions. Via oxy-cracking conditions, these solid heavy hydrocarbons do not completely oxidize to CO_2 but instead form intermediate compounds (desired products) as oxygenated hydrocarbons with different functionalities of carboxylic, sulfonic, and phenolic compounds [13]. In this case, the oxy-cracking reaction enhances the tendency of large heavy hydrocarbon molecules to disaggregate, making them more accessible to subsequent hydrogenation and cracking at lower temperatures, for the case of upgrading. The key benefit of this technology is not only the high efficiency, conversion and selectivity for desired products but also zero CO_2 emissions during the conversion, thus making the process environmentally friendly. Moreover, this technology could be applied for demineralization and desulfurization of residue streams [11]. Nevertheless, it is obvious that the developing of catalyst with high activity, selectivity, and stability is a current challenge in liquid-phase oxidation. Therefore, it is believed that the incorporation of transition metal ions, especially the copper, into frameworks of silicates would be a promising route[14]. This is because the naturally occurring silicates have confirmed to be a promising candidate as a catalyst for the oxidation reaction due to its chemical and thermal stability, and for its unique physical-chemical properties [15]. Therefore, the copper-silicate catalyst for the petcoke oxy-cracking could be a promising strategy to develop an efficient catalyst for converting the solid waste heavy hydrocarbons into humic acid analogs [8]. Herein, the oxy-cracking technology promises to provide an alternative, efficient, environmentally-friendly and cost-effective solutions to convert residual feedstocks into value added-products. Based on the oxy-cracking conditions, petcoke can be converted into different value-added products as shown schematically in Figure 1.

One of the promising products out of this technology can be found in the liquid phase as oxygenated hydrocarbons like humic materials which can be obtained at low severity reaction conditions with the presence of a catalyst. However, at severity reaction conditions and with the absence of catalyst, the formation of humic analogs is no longer exist, instead of forming smaller molecular weights which can be isolated and used as a clean fuel for power generation. Moreover, the unconverted petcoke as the residue material is expected to consist of the minerals suggesting that the proposed technique could be employed for petcoke demineralization. Finally, the gas phase remained as predominantly oxygen and an insignificant amount of CO_2. The success of oxy-cracking reaction is evaluated by making the reaction favorable toward the desired products which strongly depends on the operating temperature and pressure as well as the reaction time and the alkalinity of the solution.

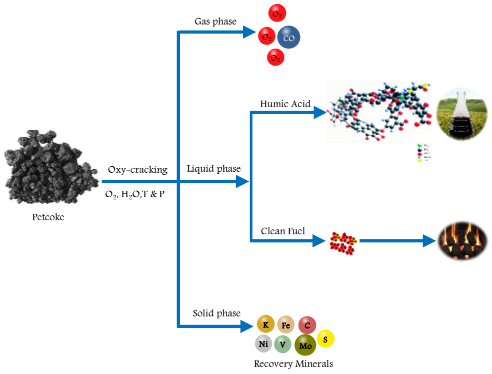

Fig. 1. Schematic representation of all possible products generated during the petcoke oxy-cracking reaction.

II. EXPERIMENTAL WORK

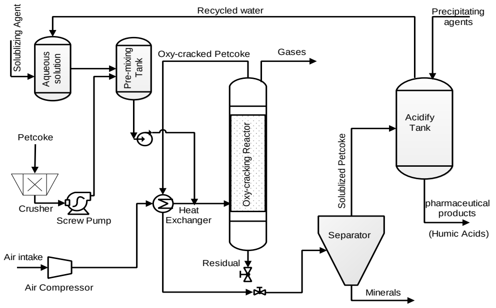

Fig. 2. Schematic representation flow diagram of petcoke oxy-cracking process.

A. *Materials*

A sample of green petcoke (Marathon Petroleum Company, Garyville, USA) was used as the source of residual feedstocks after being grinded and sieved to a particle size of 53 to 710 µm. To provide alkaline media of the reaction and adjust the solution pH, potassium hydroxide (KOH, ACS reagent, ≥85%, Sigma-Aldrich, Ontario, Canada) was used. Ultra-high purity oxygen (99.9%, Praxair, Calgary, Canada) was used as an oxidizing agent for the reaction.

B. *Experimental procedure of oxy-cracking reaction*

Figure 2 shows a schematic representation of the oxy-cracking process. The main unit is the oxy-cracker which consists of a 100 mL reactor vessel (model number 4598, Parr Instrumental Company, Moline, Il, USA). The reactor vessel is equipped with a heating oven connected to a temperature control loop, a pressure gauge and a mechanical stirrer with a speed controller. Another important unit is the pre-mixing vessel to mix the petcoke with an alkaline solution and heating them before entering the reactor vessel. Also, hot separator is needed to separate the solubilized petcoke and recover the metals. After that acid treatment is employed to precipitate the metal-free products (i.e., humic acid analog) and recycle the used water.

For understanding the reaction mechanism, a batch experiment was carried out by adding 1.0 g of solid petcoke sample into the reactor vessel containing 20 g of deionized water and 1.0 g of KOH which was subsequently pressurized with oxygen. The oxygen partial pressure was kept constant (750 psi) during all the oxy-cracking experiments. Then, the mixer was set to 1000 rpm to minimize the interfacial mass resistance. The reactor was then heated to the desired temperature. At the end of the reaction, the reactor was cooled down and connected to gas chromatography, GC (SRI 8610C, SRI Instruments) for gas analysis. Afterwards, the liquid was withdrawn and filtered for total organic carbon (TOC) analysis using a Shimadzu TOC Analyzer (TOC-L CPH/CPN). The oxy-cracked products were recovered by drying in a vacuum oven overnight at 65 °C and characterized using FTIR. Moreover, the carbon, hydrogen, and nitrogen contents for virgin and oxy-cracked petcoke samples were analyzed by combustion method using a PerkinElmer 2400 CHN analyzer (Waltham, Massachusetts, USA). The metal and sulfur contents in the virgin and oxy-cracked petcoke samples were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Moreover, the thermal behavior and oxidation of virgin, extracted oxy-cracked petcoke and their mixtures were investigated using a thermogravimetric TGA/DSC analyzer (SDT Q600, TA Instruments, Inc., New Castle, DE).

III. RESULTS AND DISCUSSIONS

A. *Catalytic and noncatalytic oxy-cracking of petcoke*

The triangular reaction pathway, as depicted in Figure 3, has been employed to describe the mechanism of the reaction using a lumped kinetic model [16]. The oxy-cracking technique involves the generation of a free hydroxyl radical (•OH) which plays an essential role in the oxidation of hydrocarbons [17]. Therefore, the oxy-cracking undergoes a parallel-consecutive reaction in which an oxidative decomposition took place in the first step producing different types of intermediates as oxygenated hydrocarbons.

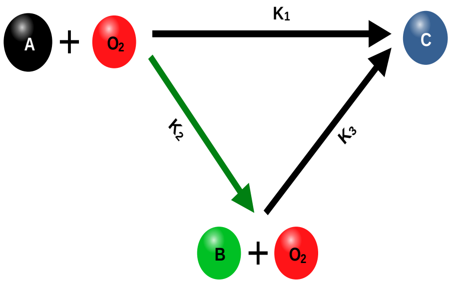

Fig. 3. Triangular reaction scheme of oxy-cracking process, A is the residual hydrocarbons, B is the humic acids analogs (oxy-cracked products, TOC), and C is the CO_2 in the gas phase and carbonates IC.

Preliminary results revealed that the reaction conversion was not significantly affected by oxygen partial pressure beyond 750 psi. Therefore, at this pressure and temperature range (180- 250 °C), the water exists only as a subcritical liquid. The effect of the temperature on the conversion and selectivity of the oxy-cracking reaction was investigated between 180 and 250 °C. The results in terms of petcoke oxy-cracking conversion and selectivity to produce both humic acids analogs (B) and CO_2 (C) without catalyst are presented in Figure 4. As seen, by increasing the temperature, the solubilization of oxy-cracked compounds in water is increased. Although the solubilization of oxygenated hydrocarbons is increased at a high temperature, the selectivity of producing CO_2 gas is also increased. Moreover, no reaction occurred at temperatures lower than 150 °C with the considered residence time. For instance, the reaction conversion was less than 30% when the temperature ranged from 150 to 180 °C at 1 h residence time.

As discussed earlier, the degree of petcoke conversion through oxy-cracking was highly influenced by the reaction temperature, residence time, oxygen pressure, and the complexity of residual feedstocks. Therefore, relatively high-energy consumption may be required for the oxy-cracking operation. Despite small emissions of CO_2 is being released especially at a high temperature, the proposed technique should be an environmentally friendly one and meet the environmental regulations. To overcome this concern, a crystalline copper silicate like cuprorivaite ($CaCuSi_4O_{10}$) with a knownthermally stable three-dimensional framework may be suitable as a catalyst for the intended application[11].

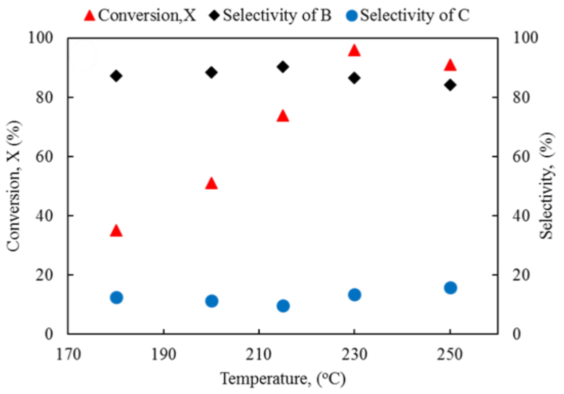

Fig. 4. Effect of the reaction temperature on the selectivity and conversion of petcoke oxy-cracking in the absence of a catalyst ($P = 750$ psi and $t = 1$ h).

The catalytic effect on oxy-cracking conversion and selectivity to produce both of desired products (B) and CO_2 (C) are presented in Figure 5. As shown, the rate of the oxy-cracking reaction conversion is significantly increased upon raising the reaction temperature. Thus, at 250 °C, ~97% petcoke conversion was reached after 1 h over the $CaCuSi_4O_{10}$ catalyst. This high conversion can be attributed to more free radical species being generated in the solution at elevated temperatures [67]. Interestingly, the reaction conversion was more than 45 % even at low temperatures of 175 °C, which is promising when compared to the non-catalytic oxy-cracking of petcoke. Although a high reaction temperature (250 °C) is not favourable in the oxy-cracking process without a catalyst, no remarkable amount of CO_2 was observed in the presence of the proposed Cu-silicate catalyst of the present study. Moreover, the selectivity to produce the desired products (B) was 99% even at the low reaction temperature of 150 °C and reaction time of 15 min.

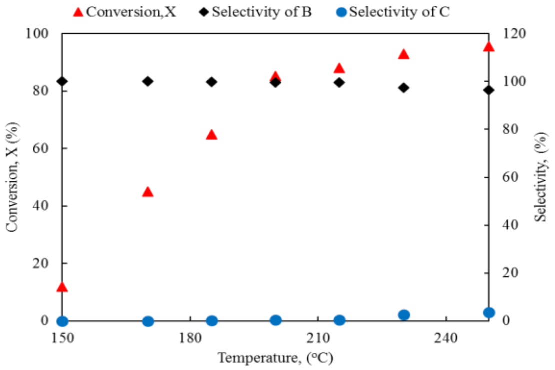

Fig. 5. Effect of the reaction temperature on the selectivity and conversion of petcoke oxy-cracking ($P = 750$, $t = 1$ h, 1000 rpm and 0.10 g of catalyst).

B. *Humic Acid production*

Humic acid has extensive application in fields like industry, agriculture, medicine, and environment protection [18]. As a kind of potential organic resources that were developed and utilized, humic acid is drawing lots of attention from the world. The global market for humic acids is expanding with over than USD$ 400 million in 2016 and will witness growth above 12% of the compound annual growth rate [19]. Based on its solubility in basic and acidic solutions, humic substances can exist in three forms humic acids (alkali-soluble and acid-insoluble), fulvic acids (alkali and acid-soluble) and humin (alkali and acid-insoluble) [20]. These substances have similar chemical fractions which contain carbon, hydrogen, oxygen, nitrogen and sulfur. However, they are different in molecular weight [21]. Conventionally, humic acid can be extracted from lignite, brown coals and humified organic materials [22]. Here, the humic acid analogs were produced from petcoke by oxy-cracking at a certain reaction. Figure 6 shows the IR-spectra of virgin and oxy-cracked petcoke and commercial humic acids (53680 humic acids, Sigma-Aldrich, Ontario, Canada). The FTIR spectrum of the oxy-cracked products is dramatically different than the original petcoke. The presence of C-H bonds vibration out-of-plane in aromatics can be assigned to the 748, 804, and 860 cm^{-1} bands in virgin petcoke. The corresponding C=C aromatic stretching vibration appears near 1580 cm^{-1}, slightly below the typical 1600 frequency, thus believed conjugated with other groups like C=C region as reported in other studies [23, 24]. The transmittance at 3040 cm^{-1} due to aromatic C-H stretching vibrations can be found in the spectra for both the original and the oxy-cracked petcoke; however, much less important in the later. Interestingly, the IR spectrum of oxy-cracked products resembles the one obtained for the commercial humic acids. As shown, the broadband centred in ~3300 cm^{-1} indicates the presence of OH groups in both samples (i.e., oxy-cracked and commercial humic acids). These functionality groups are formed due to the oxygenated species such as carboxylic functional groups. The presence of carboxylic acids (C=O) is evident as indicated by the double band centred at 1710 cm^{-1} in both samples; however, more important in the oxy-cracked products. The band at ~1800 cm^{-1} presents in the oxy-cracked sample might suggest the possibility of forming carbonyl compounds such as esters and lactones, which did not appear in the commercial humic acid sample. Calemma et al [25] reported that the absorption bands between 1600 and 1800 cm^{-1} in the humic acid obtained by coal oxidation could belong to carbonyl and carboxyl bands. Another important difference between the oxy-cracked sample and the commercial humic acid is the band at 1215 cm^{-1} corresponding to the presence of sulfur as sulfone compounds due to the high content of sulfur in virgin petcoke as presented at the small band ~1031 cm^{-1}. However, no sulfur compounds were reported in the literature for the humic acids produced from coal oxidation [26].

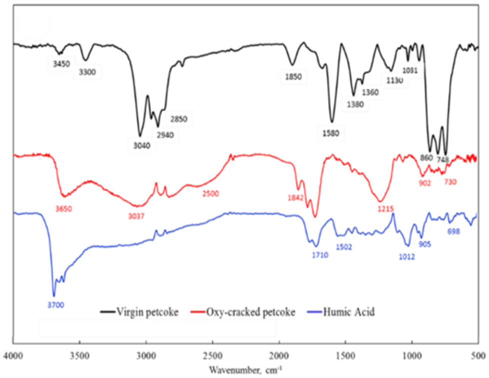

Fig. 6. FTIR spectra of the virgin petcoke, oxy-cracked products and the humic acid at 200 °C and 2 h residence time.

C. Oxy-cracked petcoke as a fuel:

The thermal behavior of oxy-cracked petcoke and their mixture with the virgin petcoke are explored using TGA. Figure 7 shows the plot of conversion degree (the fractional weight conversion, α) against the temperature for non-isothermal oxidation at three heating rates (5, 10, and 20 °C/min). As seen, the decomposition temperature of the oxy-cracked sample is much lower than virgin petcoke at any heating rate. At low heating rate, to obtain a 50% conversion of virgin petcoke a temperature of 498 °C is required while a temperature of 445 °C is needed for the oxy-cracked one to obtain the same conversion. This significant decrease in reaction temperature shows that the oxy-cracked sample is easier to oxidize as compared to the virgin petcoke. At a temperature lower than 430 °C, about 30% conversion is obtained for the oxy-cracked sample whereas no conversion is observed in the virgin petcoke at that temperature. This high conversion in the oxy-cracked sample at that temperature is attributed to the low molecular weight oxygenated compounds that formed during the oxy-cracking reaction [17].

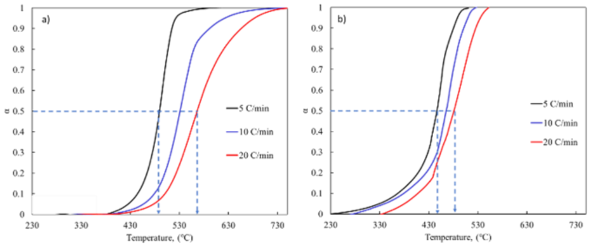

Fig. 7. The conversion percent (α) with temperature at heating rates of 5, 10 and 20 °C/min for a) virgin petcoke and b) oxy-cracked petcoke.

Figures 8 shows the rate of mass loss profiles under oxidation by air from room temperature to 800 °C at a heating rate of 10 °C/min for 0, 25, 50, and 100 wt% of oxy-cracked petcoke blended with virgin petcoke. As seen, the oxy-cracked sample is completely oxidized with the max rate at 475 °C, which is lower than that of the virgin petcoke where its oxidation occurs at a temperature around 540 °C. As expected, the profiles of blend samples lie between the curves of the virgin and oxy-cracked petcoke, and the contributions of oxy-cracked sample to these profiles can be clearly appreciated.

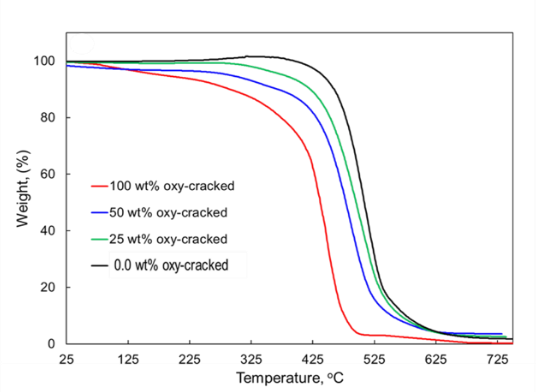

Fig. 8. TG curves for 0, 25, 50 and 100 wt% of oxy-cracked petcoke mixtures with virgin petcoke under airflow of 100 cm^3/min and heating rate of 10 °C/min.

Thus, a clear shift to the lift is observed in the mass loss profiles as the amount of oxy-cracked petcoke is increased. Also, the oxidation temperature of the blend is decreased with increasing the weight of oxy-cracking content in the blend. Therefore, blending virgin petcoke with oxy-cracked petcoke would have significant impacts on the performance of petcoke as a fuel not only in enhancing the ignition condition and maximum burning rate but also low environmental impact due to the low contribution of SOx and NOx. These blends will provide a technically sound, cost-effective and environmentally friendly burring of petcoke as fuel in the power generation as an alternative to coal, thus overcoming the environmental limitations on combustion of petcoke and reducing the dependence on the coal as well.

D. *Metal recovery*

In addition to the potential collaboration of this technology for producing humic acid materials, the reject metals, such as vanadium which can be used in flow battery applications, provide specific opportunities for diversification in economy streams. This is because the high metal content is concentrated in the residual feedstock like petcoke such as vanadium, iron and nickel in addition to the sulfur content. These metals strongly depend on the nature and the coking process of crude oil, which can be found as organic and inorganic compounds [27]. The presence of metals could occur as metal chelates or porphyrines[28]. However, other metals are not chemically bonded but intercalated in the petcoke structure, as mineral salts normally found as part of ashes[29]. As discussed earlier, the petcoke sample is converted into oxygenated hydrocarbons which is soluble in water, as humic acids analog. However, at certain reaction conditions, a small amount of solid residue (unreacted petcoke) was left over after the reaction and precipitated in the bottom of the reactor vessel, where the minerals are the major components of this residue.

TABLE 1. Elemental content in the virgin, oxy-cracked and residue petcoke at temperature 215 °C, pressure 750 psi and time 2 h.

Elements	**Virgin petcoke (wt%)**	**Residual (wt%)**	**Oxy cracked (wt%)**
C	84.47	55.71	64.04
H	3.8	3.87	3.97
N	1.5	4.84	1.63
S	4.46	19.92	1.96
V	0.08	0.19	0.06
Ni	0.03	0.16	0.01
Fe	0.06	1.85	0.01
Mo	0.01	0.02	0.00
Co	0.05	0.07	0.00
O*	5.55	13.35	28.32

* Estimated by the difference

Table 1 shows the elemental analysis for the virgin petcoke sample, oxy-cracked sample and the remaining solids (residue) after the reaction that was carried out at 215°C for 2 h. As seen, the primary heteroatoms and metals present in the virgin petcoke sample are sulfur and metals like vanadium, nickel, iron, cobalt and molybdenum. The carbon, sulfur, hydrogen and nitrogen content in the oxy-cracked sample were less than that of virgin petcoke which can be explained due to partial oxidation of petcoke to form oxygenated hydrocarbons. Moreover, most of the metals, sulfur and nitrogen were concentrated in the residual petcoke. The metal contents such as vanadium, iron, nickel, cobalt and molybdenum were found to be higher in the residue compared with virgin and oxy-cracked petcoke. It can be concluded from these findings that the unreacted petcoke which left over after reaction is mainly a concentrated mineral with some heteroatoms bonded with carbon skeleton. These findings suggest that the oxy-cracking process could be a useful technique for petcoke demineralization and desulfurization.

IV. CONCLUSION

A new approach for waste hydrocarbons conversion into valuable products was explored in this study by using oxy-cracking process which is operating at mild temperature and pressure in an aqueous alkaline medium. A copper-silicate material was successfully synthesized in-house and tested as a new catalyst for the oxy-cracking reaction. A high reaction conversion and high selectivity to water solubilized products with the almost zero emissions of CO_2 were obtained even at high reaction temperatures. The oxy-cracked compounds solubilized in water during the reaction were characterized using FTIR and the main species were carboxylic, carbonyl, phenolic, and sulfonic functions which are responsible for humic acid compounds. Interestingly, the metal content was found to be insignificant in the oxy-cracked products suggesting the possibility of the oxy-cracking technique as a new feasible process for demineralization of petroleum coke. The thermal reactivity of oxy-cracked products as a potential alternative fuel for power generation was investigated using the thermo-oxidative decomposition analysis by TGA. The oxidation results showed that the oxy-cracked product is easier and faster to oxidize compared to the virgin petcoke. These findings suggest that the use of oxy-cracked product as a fuel for power generation would be safer, more efficient, and less polluting than the virgin petcoke.

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