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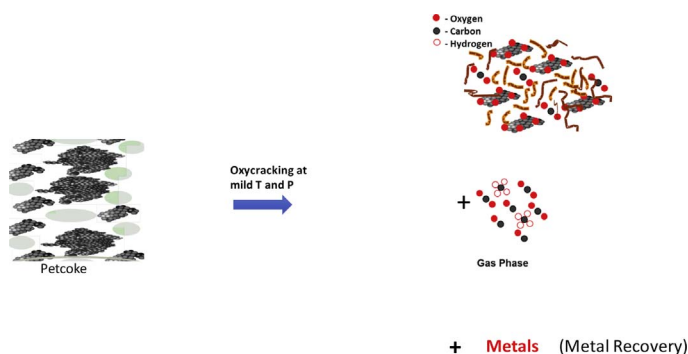
# Conversion of petroleum coke into valuable products using oxy-cracking technique



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## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Oxy-cracking  
Oxidation  
Cracking  
Petroleum coke  
Solubility  
Reaction kinetics  
Deminerlization

## ABSTRACT

The global production of residual feedstock has reached 150 million metric tons per annum and is expected to increase in the future due to the progressively increasing heavier nature of the crudes. Petroleum coke (petcoke), one of these residues, is a solid-rich carbon typically produced during the upgrading of heavy oil and delay coking of vacuum residue in the refinery. Finding an alternative technique to treat this massive amount of petcoke is highly needed as the conventional processes like gasification and combustion have limitations in terms of efficiency and environmental friendliness. In this study, an oxy-cracking technique, which is a combination of cracking and oxidation reactions, is conducted as an alternative approach for petcoke utilization. The reaction is conducted in a Parr reactor where petcoke particles are solubilized in an aqueous alkaline medium and partially oxidized under mild operating temperature and pressure. Several operating conditions on petcoke oxy-cracking were investigated, such as temperature, oxygen pressure, reaction time, particle size and mixing rate to optimize the solubility and selectivity of oxy-cracked products. The results showed that the temperature and the residence time are the two major important parameters that affect the reaction conversion and selectivity. This enabled us to propose a reaction pathway based on the radical mechanism to describe the kinetic behavior of petcoke. Reaction kinetics indicated that petcoke oxidation undergoes a parallel-consecutive reaction in which an oxidative decomposition took place in the first step producing different oxidized intermediates. The oxy-cracked petcoke was characterized by FTIR, XPS and NMR analyses. The oxy-cracked products were found to contain carboxylic, carbonyl, phenolic, and sulfonic functions. Moreover, the elemental analysis showed that most of the metals remained in the residue, suggesting that the proposed technique could be employed for petcoke deminerlization.

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## 1. Introduction

Coking process is applied to upgrade bitumen, petroleum residue, vacuum residue, solvent-deasphalter pitch, rich asphaltenes and resin fuel, to more desirable products like LPG, naphtha, diesel and gas oil [1,2]. During the coking process, fuel gas and petroleum coke (petcoke) are also produced [3–5]. This coking process is typically a thermal cracking process in which the H/C atomic ratio of the product is increased by a carbon rejection mechanism [6]. Hence, multi-reactions that undergo a free radical mechanism are coupled together with cracking and polymerization reactions [7]. Cracking reactions produce gas and liquid products which are the most valuable ones, while radical polymerization reactions produce petcoke [8]. This petcoke is a rock-like structure mainly made out of carbon, hydrogen, nitrogen, sulfur and some metals. The global production of petcoke has reached about 150 million metric tons per annum. The North America alone produces about 70% out of the total petcoke capacity [9]. In 2014, Canada's oil sands reserves amounted to approximately 166 billion barrels, the third largest after Venezuela and Saudi Arabia [10,11]. In fact, in 2016, nearly 80 million tons of solid waste hydrocarbons (petcoke) were being stockpiled in Alberta as a by-product of the Canadian oil sands industries [9]. Consequently, approximately two-thirds of the produced petcoke have been accumulated and stored on-site for many years [12,13]. Due to limited markets and minimal use for this commodity, the stockpile is growing at a rate of about 4 million tons a year [14,15].

Petcoke is also generated in refineries through either delayed or fluid coking processes at high temperature and pressure. These coking processes are highly dependent upon their thermal treatments [4]. Delayed coking commonly occurs at a temperature range of 415–450 °C, whereas fluid coking uses higher temperatures ranging from 480 to 565 °C [8,16–18]. Generally, the produced petcoke has a high carbon content (80–85 wt%) consisting of polycyclic aromatic hydrocarbons with low hydrogen content. It is worth noting that petcoke has a lower amount of ash, moisture, and volatiles compared to coal [8]. However, it contains high amounts of sulfur (5–7 wt%) and vanadium (~700 ppm), which can severely impact human and animal health [19]. Additionally, dust emissions from petcoke piles impose a serious threat to people in the vicinity [19,20]. Furthermore, petcoke can be classified into calcined and green coke, where the latter is the initial product of the coking process that can be used as fuel in metallurgical and gasification processes [20]. Calcined coke, on the other hand, is produced by treating the green coke at a high temperature between 1200 and 1350 °C [20,21]. Depending upon its physical properties, structure, and morphology, the calcined coke can be formed as a sponge, shot and needle coke [22]. Oil sands companies often use different coking techniques [23]. Suncor Energy's coking process, for example, produces “delayed” petcoke, which has a sponge-like structure [24]. In contrast, Syncrude's coke is known as “fluid” coke and it has highly-graphitized layers and is often described to have an onion-like structure [23,25].

Petcoke has a high calorific value, as indicated from the literature at approximately ~37 MJ/kg, which makes it a valuable fuel resource for future application [26,27]. Therefore, alternative uses of this material could be considered and of paramount importance. Recently, a number of researchers have investigated the potential use of petcoke as a precursor for production of activated carbon due to its high carbon content [5,28,29]. Meanwhile, many studies have demonstrated that petcoke can be thermally, physically and chemically activated, in the presence of a reagent to produce activated carbon with the high specific surface area (~500–1500 m<sup>2</sup>/g) [28,30–33]. However, the costs of generating activated carbon through either physical or chemical activation processes tend to be quite high, especially when the yield does not balance the generating costs, thus the total investment cost would be challenging for large-scale industries [34,35]. Moreover, the corrosive nature of the chemical activating agents has negative environmental impacts and often limits its application [32].

Alternative applications have included the use of petcoke for heat generation purposes, such as combustion and gasification [15,17,36]. Hence, petcoke could be an alternative fuel in power generation due to its higher heating value and lower price than coal. Although petcoke is a potential combustible as a fuel source, combustion process would invariably produce large quantities of sulfur dioxide (SO<sub>2</sub>) [37]. Gasification process, on the other hand, was implemented to produce syngas and hydrogen at high temperatures (800–800 °C) and pressures (145–1450 psi) [36,38]. Although the gasification process captures more energy content, it is more capital intensive [39–42]. Additionally, gasification is not deemed to be a reliable technology for the treatment of these waste hydrocarbons, primarily due to the decline in current gas prices and the recent increase in shale gas production [43,44].

Despite all the attempts and processes that have been proposed in the industry to treat and reduce the amount of these waste hydrocarbons, a massive amount of petcoke is still present. Therefore, the development of an efficient and environmentally friendly technology is still a challenging and of paramount importance. Recently, our research group has introduced an oxy-cracking technique for converting heavy solid hydrocarbons into valuable products using a model residual feedstock exemplified by Quinolin-65 (Q-65) and n-C<sub>7</sub> asphaltenes [40,45]. This technique is a combination of oxidation and cracking reactions in an aqueous alkaline media is inspired by asphaltenes oxidation and ozonolysis studies [46–51]. Through the oxy-cracking process, a new reaction pathway is offered in an aqueous alkaline medium, at mild temperatures (170–230 °C) and pressures (500–750 psi). Importantly, the oxy-cracking process has a high efficiency to convert the solid waste hydrocarbons into valuable light commodity products [40,45]. The oxy-cracked materials (i.e., not completely oxidized) become soluble in water via oxygen incorporation due to the polar functionalization of the aromatic edges and paraffinic terminal carbons. Hence, the oxy-cracking undergoes a parallel-consecutive reaction in which an oxidative decomposition took place in the first step producing different aromatic intermediates. Those intermediates could be carboxylic acids and their corresponding salts, or other products [45,52,53]. Because of the high solubility and selectivity of oxy-cracked products in the alkaline medium and the insignificant amount of produced CO<sub>2</sub>, the oxy-cracking process could be considered an environmentally friendly one. Similarly, a theoretical and experimental study on oxy-cracking of the Quinolin-65 (Q-65) molecule as a model molecule for residual feedstocks has recently confirmed that the attacks of the hydroxyl radical (·OH) plays an important role in the oxy-cracking reaction of Q-65 and n-C<sub>7</sub> asphaltenes [40,45].

Herein, in this study, we are applying the oxy-cracking technique as a new approach for converting petcoke into valuable commodity products by solubilizing it in water under alkaline conditions. The maximum solubilization and selectivity of oxy-cracked petcoke (i.e., desired products) in alkaline media with minimal emission of CO<sub>2</sub> are the main target. Eventually, at the end of the reaction, the oxy-cracked products are characterized using Fourier transformed infrared spectroscopy (FTIR), total organic carbon analysis (TOC), nuclear magnetic resonance (NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) techniques. The gas emissions generated during the oxy-cracking process are also identified using gas chromatography (GC). The non-reacted solid residue is also analyzed using elemental analysis and FTIR as well. Moreover, the generalized “triangular” lumped kinetic model [54] is used here to determine the reaction kinetics parameters and the potential mechanism for the oxy-cracking of petcoke. It is expected that this study opens a better outlook about the use of the oxy-cracking process in the oil industry, mainly in treating residual feedstock such as petcoke and the like.

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