



Research paper

Impacts of amount of chemical agent and addition of steam for activation of petroleum coke with KOH or NaOH

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ABSTRACT

There are millions of tonnes of petroleum coke stockpiled worldwide, but to take advantage of this potential resource, a better understanding of how to activate this feedstock with less waste is required. The impact of steam addition during chemical activation of petroleum coke with a high sulfur content (~6.5 wt%) was evaluated with two chemical agents (KOH and NaOH), chemical molar ratios (from 0.12 to 1.02 or mass ratios from 0.5 to 3) and activation times (0 to 120 min) at 1073 K. Based on the yield and total pore volume developed, co-activation of KOH and steam was an effective way to reduce the amount of chemical agent required, while widening the pores from ~1 nm to up to 4 nm. In contrast, the addition of steam to the activation with NaOH resulted in less pore development and essentially no change in the pore size. At the activation conditions, there is likely a molten phase around the particles that slows steam gasification and has a composition that changes with the introduction of steam.

1. Introduction

Petroleum coke (petcoke) is a carbon-rich solid byproduct from crude oil refineries. Crude bitumen production was 4.2 million barrels per day in 2018 from western Canadian reserves, and is estimated to grow to 6.2 million barrels per day in 2035 [1]. High grade petcoke is widely used in the metallurgical industry and in the production of electrodes. Over 80% of the petcoke produced worldwide, however, is low grade (i.e., 5–7 wt% sulfur and heavy metals including nickel and vanadium), which prevents it from being used as a traditional fuel due to environmental concerns [2]. Currently, the surplus petcoke is stockpiled near refinery and upgrading facilities [3]. These stockpiles represent a potential hazard for public health since petcoke particulates can be transported in the form of airborne dust [4,5], and the stockpiles occupy considerable space that could be otherwise utilized. Given these issues, there is interest in valorizing this by-product. Previous work has shown the potential of using petcoke as a starting material to produce adsorbents and catalyst supports [6–9].

Petcoke is a non-porous solid, which generally must be activated before use for the above-mentioned applications [6,7,10–12]. In fact, although an economic evaluation on minimizing production costs of activated carbon (AC) found that petcoke is the most promising raw material among several carbonaceous materials including wood, used tires, carbon black, charcoal, and lignite, its biggest challenge is its non-

porous nature [13]. Activation generally involves oxidation and/or intercalation of species within the structure [14,15]. In the former process, solid carbon is transformed into CO and CO₂, creating pores, while in the latter process, a species, generally a metal, acts as a spacer and increases the pore volume by widening the distance between the carbon layers [16]. The advantage of intercalation is the increase in porosity without carbon consumption, resulting in higher yields and lower emissions than oxidation. In either method, the produced AC is washed to remove excess reactants and ensure that the pores are accessible.

The Kansai Coke and Chemicals Company developed MAXSORB, a high-surface-area (3100 m²/g as measured by the BET model) AC derived from low grade petcoke activated with KOH [8]. Even though a pore volume of 1.76 cm³/g was obtained using a KOH:petcoke mass ratio of five, the higher chemical usage led to low yields (< 30%), higher production costs, and more waste. Generally a mass ratio of at least three is required to develop significant porosity (pore volume above 0.8 cm³/g with activation at 1073 K) in AC from petcoke [10,17–21]. Various approaches have been tried to reduce the amount of chemical agent required. Deng et al. [22] treated low grade petcoke with HClO₄ to induce intercalation during activation with KOH at 1073 K. The resulting AC had a surface area (~3000 cm²/g) that was similar to AC prepared with a KOH:petcoke mass ratio of five. Wu et al. [23] activated low grade petcoke with KOH (mass ratio of two) and

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steam at 1073 K for 25 min, and produced AC with surface areas of 2500–3000 m²/g but with low yields of 25–30%. The authors stated that the porosity created during the catalytic steam gasification promoted the diffusion of steam. The challenge, therefore, is to produce some porosity without consuming too much of the feed.

Lillo-Ródenas et al. compared the activation of non-porous anthracite with KOH and NaOH at 1003 K and found that with a mass ratio higher than one, KOH produced more pore volume than NaOH [24]. In other studies involving the NaOH activation of different feeds, including non-porous arthracite [25], plum kernels [26], and corncobs [27], higher pore volumes and pore sizes were obtained as the mass ratio of chemical agent to feed increased from one upwards, but none of these studies discussed the process of activation in depth. While there are many studies on gasification, in which the goal is to consume all of the feed, co-activation (e.g., simultaneous chemical (H₃PO₄, KOH, ZnCl₂) and physical activation (CO₂, steam, air)) has only been studied by a few groups. The synergistic effect of chemical and physical agents (2–5 h co-activation from 873 to 1173 K) enhanced the pore volume and surface area on various materials including coconut shells [28], palm stones [28], *Zizania latifolia* leaves [29], and woody biomass [30] but resulted in yields < 30%. The interaction between the chemical and physical agents is not well understood, especially as most studies choose a fixed amount of the agents and vary the other parameters (temperature, time, etc.). In addition, the porosity of the feedstock influences pore development [18,31] so the results that have been obtained with porous lignocellulosic materials may not be applicable to other feedstocks. In our previous study of the activation of petcoke [21], in which the goal was to maximize mesoporosity, the addition of steam created pores up to 4 nm, but the yields were always lower with co-activation or steam activation after chemical activation (with washing at room temperature in between the steps). The chemical agent (KOH or NaOH) to petcoke mass ratio was three for all experiments.

In many other studies, the yields obtained and the wastes created by the methods used have been ignored. On an industrial scale, washing away 75% of the reactants (i.e., for a 3:1 mass ratio of chemical agent to carbon feed) may not be economically feasible. Thus, the impact of changing the chemical agent to petcoke ratio was the main impetus for the current study. With the goal of reducing the amount of chemical agent required while maintaining the desired properties (porosity, pore size, and yield), we have also obtained a better understanding of the activation process and the impact of steam addition. Specifically, a low-grade petcoke feed was activated with various combinations of steam and KOH or NaOH at 1073 K, with mass ratios of hydroxide to petcoke ranging from 0.5 to 3. The samples were analyzed with N₂ adsorption and scanning electron microscopy.

2. Materials and methods

2.1. Sample preparation

Delayed petcoke from Suncor Energy Inc., Alberta, Canada, which contains 84 wt% C, 6.5 wt% S, and 3.7 wt% ash (see reference [19] for full proximate and ultimate analyses) was used for this study. The petcoke was ground and sieved to particles between 150 and 300 µm, and then 2.5 g were mixed with NaOH (97%, Sigma-Aldrich Inc., St. Louis, USA) or KOH (85%, Alfa Aesar, Hey-sham, UK) in a mortar and pestle with mass ratios of chemical agent:carbon from 0.5–3. Petcoke contains 84 wt% carbon and this value was used to determine the appropriate amount of petcoke to use for a specific ratio. The corresponding molar ratios are listed in Table 1. Although mass ratios are commonly reported in the literature, the molar ratios are more instructive when considering the chemical reactions. The samples are named according to the molar ratio and chemical agent used (i.e., 0.12KOH refers to a sample activated with a molar ratio of KOH to carbon of 0.12). For chemical activation, the mixtures were placed in a ceramic boat, which was then placed inside a horizontal furnace and

Table 1

Equivalent molar ratios for different mass ratios of chemical agent:carbon.

Mass ratio	Molar ratio	
	NaOH	KOH
0.5	0.17	0.12
1	0.34	0.24
2	0.68	0.48
3	1.02	0.72

heated under flowing nitrogen (100 cm³/min) at a rate of 5 K/min from room temperature to 1073 K, and holding at the final temperature for 0 or 30 min. The produced AC was cooled to room temperature, then washed with 250 cm³ of 1 mol HCl solution and de-ionized water until the pH of the washing solution was neutral. Thermogravimetric analysis of the samples after washing indicated that the washed AC samples contained < 1 wt% ash.

For co-activation (i.e., activation with a chemical agent and steam), steam (~70 vol% in N₂, 600 mL/min) was fed into the furnace when the sample temperature reached 1073 K. This amount of steam was sufficient for activation without gasifying too much of the feed. In the presence of steam, activation times of 15 min, 30 min, 45 min, 60 min, 90 min and 120 min were tested. Samples produced from co-activation have “/St” added to the name. For example, 0.48KOH/St refers to a sample co-activated with KOH and steam with a molar ratio of KOH to carbon of 0.48.

2.2. Sample characterization

N₂ adsorption was carried out on an adsorption apparatus (TriStar II Plus, Micromeritics, USA) at 77 K. The samples were degassed at 423 K for 5 h before analysis. The total pore volume was obtained at relative pressures of 0.97 on the isotherms, and the pore size distributions (PSD) were determined with the SAIEUS program (Micromeritics). The best fits to the isotherms were obtained with the 2-Dimensional Non-Local Density Functional Theory with heterogeneous surface (2D-NLDFT-HS) model for samples activated with KOH, and the 2D-NLDFT (As = 6, As refers to the aspect ratio) model for samples activated with NaOH. More details on these methods and their applications to carbon-based materials are available elsewhere [32].

The yield was calculated according to Eq. (1) in which m_i and m_f are the initial and final masses, respectively. The pore volume per gram of petcoke was obtained by multiplying the total pore volume by the yield.

$$\text{Yield (\%)} = \frac{m_f}{m_i} * 100\% \quad (1)$$

For scanning electron microscopy (SEM) analysis, samples were placed on a holder using carbon tape and then imaged (FEI Quanta 250 field emission SEM, Hillsboro, Oregon, USA). For sample cross sections, the selected sample was embedded in an epoxy resin (Devcon) by mixing approximately three parts of resin with one part of sample by volume. A glass Pasteur pipette of 0.75 cm (internal diameter) was filled with the mixture and allowed to solidify overnight. The pipette was dipped into liquid N₂ to separate the glass pipette from the solid resin. The resin was then fractured to expose the embedded sample, which was mounted on carbon tape and analyzed in the SEM.

3. Results and discussion

3.1. Impacts of type and amount of chemical agent

The total pore volumes and yields as a function of the amount of chemical agent are shown in Figs. 1 and 2 for KOH and NaOH, respectively. Chemical activation generally produced microporosity (> 70%, the specific pore size distributions will be discussed later). In

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