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Adsorptive Denitrogenation of Fuel by Oil Palm Shells as Low Cost Adsorbents

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Abstract: This study reviews the suitability and effectiveness of oil palm shells as low cost adsorbents via physically activation with carbon dioxide as an adsorbent for denitrogenation of fuel under different concentrations. With hydrogen, high temperature and pressure, hydro-denitrogenation (HDN) is used to remove Nitrogen Containing Compounds (NCCs). However, the cost of HDN is increasing rapidly due to the increasing concentration of NCCs in fossil fuels. NCCs compete with sulfur compounds on the active sites of catalysts in the conventional process. Therefore, NCCs should be removed as much as possible. Thus, searching for an alternative process to remove NCCs in a cost efficient manner is very important.

Key words: Denitrogenation, nitrogen containing compounds, oil palm shells, adsorbents

INTRODUCTION

Crude oil is the product of the remains of prehistoric plants and animals, buried in the primeval mud of swamps, lakes and oceans. Over the centuries, layers of mud and organic debris were subjected to enormous pressures and high temperatures and a petroleum saturated rock was formed.

The nitrogen content of crude oil ranges from trace amounts to 0.9% by weight. The bulk of the fractions that boils below about 200°C are basically nitrogen compounds. Quinolines, benzoquinolines and carbazoles are the most important families of organonitrogen compounds in the aromatic fractions of crude oils (Bakel and Philp, 1990). Pyridines found in crude oils are categorized as basic nitrogen compounds, respectively. Pyrroles, indoles and carbozole found in crude oils are non-basic nitrogen components.

Due to presence of some organic nitrogen species, the efficiency of a catalytic process decreases and the instability of the related products of crude oil increases during storage (Drushel and Sommers, 1966). Moreover, before carrying out the hydro-desulfurization (HDS) process, Nitrogen Containing Compounds (NCCs) should be removed from the fuels because they hamper the catalytic process of HDS by competing with Sulfur Containing Compounds (SCCs) for the active sites and reduce the activity of the catalysts (Almarri, 2009). Historically, NCCs have been removed by hydro denitrogenation (HDN) in the presence of expensive hydrogen at high temperature and pressure (Hernandez-Maldonado and Yang, 2004); however, the cost of HDN is also increasing rapidly due to the increasing concentration of NCCs in fossil fuels. Moreover, compared to HDS, HDN is a kinetically slow process (Eijsbouts et al., 1991). Therefore, searching for an alternative process to remove NCCs in a cost efficient manner is very important.

There is only a small fraction of nitrogen content in crude oil, the rest consists mainly of hydrocarbons. However, it is impractical to apply the adsorptive denitrogenation method directly into the crude oil. This is because all other compounds present in the crude oil, may adsorb on the Activated Carbon (AC). Therefore, introduction of the adsorptive denitrogenation should be after the crude oil has been converted into fuel or any other product of distilled crude oil.

NITROGEN REMOVAL FROM FUEL

Sulfur removal improves after removal of nitrogen compounds (N-compounds) from real feedstock. This is due to irreversible adsorption of NCCs on acidic sites in hydrodesulfurization catalysts which may be avoided (Laredo et al., 2013). By using quinolone, indole and carbazole in the hydrodesulfurization of dibenzothiophene, it has been found that the inhibiting effect of the NCCs increased in the order of carbazole, quinolone then indole. Even at a low concentration of 5 ppm, the inhibiting effect of the NCCs has been detected to be very strong (Laredo et al., 2001).

Many studies have proved that the removal of nitrogen can improve hydrodesulfurization of straight run gas oil. They did so by spiking gas oil with quinolone and

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it has been observed a decrease in the rate of sulfur removal (Jones *et al.*, 1995). A removal of 80% of NCCs resulted in much higher reactivates of sulfur compounds in hydrodesulfurization reaction (Choi *et al.*, 2004). Generally, it has been acknowledged that the NCCs and refractory SCCs compete for the same type of catalytic active sites, so that the adsorption of N-compounds prior to the hydrodesulfurization process improves not only hydrodenitrogenation but also hydrodesulfurization (Laredo *et al.*, 2013).

Adsorptive nitrogen removal from fuel: Several types of solid materials have been used for nitrogen removal. The materials that have been tested in batch system using either model or real feed are, π-acceptor molecules, methyl viologen aluminum silicate, activated alumina, activated carbons, mesoporous molecular sieves and metal organic frameworks.

To remove neutral heterocyclic NCCs selectively from diesel feed, a charge transfer mechanism, by π-acceptor molecules covalently attached on hydrophilic support, were used (Macaud *et al.*, 2004). However, desulfurization and denitrogenation of light oils through formation of a charge transfer complex was tested using methyl viologen-modified aluminosilicate adsorbent (Shiraishi *et al.*, 2004). In this study, only the denitrogenation was achieved successfully, due to low ionization potential of NCCs, whereas aromatic hydrocarbons forming the charge transfer complex competed with the desulfurization process.

AC revealed a greater capacity than activated alumina samples in the removal of NCCs (Almarri, 2009). A recent study has been found that oxygen functionality of the AC may play an important role in defining the adsorption capacity of NCCs (Wen *et al.*, 2010). It was mentioned that acidic functional group such as carboxyl and carboxylic anhydride supported the adsorption of quinolone. Whereas, basic oxygen-containing groups, such as carbonyl and quinone groups, supported the adsorption of indole. In the same study, it has been found that the total nitrogen adsorbed on the AC was higher than sulfer and quinolone was removed at a higher level than indole and carbazole.

Ti-HMS is a good mesoporous molecular sieve adsorbent for the adsorptive denitrogenation of fuel. The thermodynamic function shows that the adsorption of NCCs on Ti-HMS is a spontaneous physical process (Zhang *et al.*, 2010). Lithium-modified mesoporous silica adsorbent was prepared in order to selectively remove NCCs from residue hydrodesulfurization diesel. The adsorbent showed a greater adsorption affinity for NCCs than for SCCs (Koriakin *et al.*, 2010). MIL-101, a

Metal-Organic Framework (MOF), showed a remarkable adsorption capability and selectivity towards N-compounds from straight run gas oil, light cycle oil and model mixtures (Nuzhdin *et al.*, 2010). Coordination of nitrogen atoms to Cr^{III} centers of the metal-organic framework clarifies this phenomenon, whereas adsorption of other aromatics occurs mainly due to the stacking interaction.

Low cost adsorbents: Waste products for low cost adsorbents are great alternatives of AC, because it minimizes waste which can be recovered and be reused. Carbonaceous material, such as AC, exhibits high degree of porosity and extended inter particulate surface area (Bansal *et al.*, 1988). A typical AC has high surface area (600-2000 $m^2 g^{-1}$) and well-defined microporous structure (average pore opening is about 1.5 nm) (Streat *et al.*, 1995).

Several raw materials from waste products have been tested for the preparation of AC. Many wastes from industries and agriculture are high in carbon content and offer substantial possibility for the preparation of carbonaceous chars. Also, it can be further activated to obtain porous adsorbents (Ali *et al.*, 2012). House hold wastes such as fruit waste from olive stone, almond shells, apricot stones, peach stones and palm fruit bunch have surface area that ranges between 90 and 1550 $m^2 g^{-1}$ when evaluated by applying the Langmuir equation (Rodriguez-Reinoso *et al.*, 1982).

Coconut shells are also one of the house hold wastes that can be one of the alternatives for AC. It is currently responsible for approximately 18% in the global production of commercial AC. The carbon prepared from coconut shell has surface area to be 800 $m^2 g^{-1}$ and contains high adsorbing properties (Banerjee *et al.*, 1976). Similar research was conducted by Laine *et al.* (1989). In this study, carbon was prepared from Vanezuelan coconut and it was chemically activated. The shells were impregnated with H_3PO_4 followed by a one-step carbonization/activation at 450°C and the result of the surface area was 1200 $m^2 g^{-1}$.

Besides house hold waste, agricultural products can also be prepared as an AC. Because of the high tannin content in the bark of timber, it can be used as a possible adsorbent. This is because of active specie in the adsorption process which is the polyhydroxyl group of tannin (Ali *et al.*, 2012). The AC that was prepared from carbonized slash pine bark has surface area, average micropore and mesopore diameter and micropore volume 332 $m^2 g^{-1}$, 21.7 Å and 0.125 $cm^3 g^{-1}$, respectively (Edgehill and Lu, 1998). Chromium tanned leather waste as low cast adsorbent is high in ash (Cr_2O_3) content and it

Table 1: Low cost adsorbents and their surface area

Low cost adsorbents	Surface area ($m^2\,g^{-1}$)	Reference
Olive stone, almond shells, apricot stones, peach stones and palm fruit bunch	90-1550	Rodriguez-Reinoso and Molina-Sabio (1992)
Coconut shells	800	Banerjee *et al.* (1976)
Vanezuelan coconut (impregnated with H_3PO_4)	1200	Laine *et al.* (1989)
Carbonized slash pine bark	332	Edgehill and Lu (1998)
Chromium tanned leather	108	Martinez-Sanchez *et al.* (1989)
Palm tree cobs	23-1078	Renouprez and Avom (1988)

has 22-69% w/w. It also has a maximum surface area of $108\ m^2\,g^{-1}$. The AC prepared from palm tree cobs, a waste from the palm oil industry in Cameroon, has a surface area ranging from $23\text{-}1078\ m^2\,g^{-1}$ (Renouprez and Avom, 1988).

The future of low cost adsorbents is very promising in developing and under developed countries because of the universal and inexpensive natures of adsorption technology. However, the exhausted adsorbents are an issue that has yet to be solved. Ali *et al.* (2012) has suggested that the removed pollutants should either be recycled or buried deep into the soil. Table 1 summarizes the list of low cost adsorbents and their surface area accordingly for adsorption technology.

Oil-palm shell as alternative adsorbent: It is well known that the removal of gaseous and aqueous pollutants occur by adsorption with AC (Cheremisinoff and Cheremisinoff, 1993). Commercial AC can be contrived from numerous carbonaceous precursors. However, since the price of commercial AC is increasing significantly, interests are growing in the use of low cost adsorbents and copiously available lignocellulosic materials as precursors for the preparation of activated carbon (Derbyshire *et al.*, 1998). For low cost adsorbents, it should have similar or better characteristics of the commercial AC. The characteristics of low cost adsorbents should be of high density, relatively high carbon content and low ash content in order to prepare a high-quality AC. It should be also able to resist high thermal stability, high abrasion resistance as well as small pore diameters which will give a higher exposed surface area (Ali *et al.*, 2012). It should also be cheap, easy to obtain and in abundant in nature and oil-palm shells are just the right precursor to fit the requirements.

To obtain carbons with high surface area and narrow micropore distribution, chemical activation has shown to be very efficient. However, most of the chemicals used are not always environmentally friendly. Alkali hydroxides such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are hazardous, expensive and corrosive (Lillo-Rodenas *et al.*, 2004) and $ZnCl_2$ is unfriendly to the environment and create water disposal problems (Guo and Lua, 2002). Therefore, a cleaner and cheaper

alternative needs to be approached in order to obtain carbons with high surface area and narrow micropore distribution, by activating the char of the oil-palm shells with carbon dioxide (CO_2).

In the preparation of the AC from oil-palm shells (Guo and Lua, 2002), after carbonization, by using the FTIR spectrometer, the char displayed the surface functional groups of ketone, quinone and aromatic rings. The AC obtained by flushing the char with CO_2 and high temperature, the ketonic group were absent due to their thermal instabilities at high temperature. However, when the adsorptive capacity for nitrogen dioxide (NO_2) and ammonia (NH_3) was tested, the Brunauer, Emmett and Teller (BET) surface area was found to be linearly proportional, this is because the surface functional groups of the activated carbon from the oil-palm shell were generally neutral.

AC, prepared from oil-palm shells, are highly porous with sufficiently high densities. This means that it minimizes the carbon losses during handling and conveying of these materials in industrial applications. The surface of the AC prepared from oil-palm shells was studied using the SEM micrographs and it was found that there were no more lignocellulosic structures on the surface but many small cavities over the surface, forming a system of advance pore network. With these findings, it can be infered that the AC was expected to have large BET and micropore surface area. This makes it to be a suitable as effective adsorbents (Guo and Lua, 2002).

Large BET and micropore surface area make an ideal adsorbent. However, the adsorptive capacity that is related to the specific pore surface area plays the most important part in the property of the activated carbon. Therefore, it implies that the higher the pore surface area of the AC, the larger the adsorptive capacity (Guo and Lua, 2002).

REGENERATION

Spent activated adsorbent must be regenerated before reuse, since the active site of the pores of the AC are blocked or being adsorbed by the adsorbents and needs to be regenerated in order to break the bonds

between the adsorbents and the adsorbates. Regeneration of spent AC is not only important for the purpose of reusability but also when it comes to disposing it. The adorbed adsorbates from the adsorbent could be considered as hazardous waste and it requires special treatment facility (Sheintuch and Matatov-Meytal, 1999).

The first method ever discovered for regenerating spent AC in a commercial scale was in the year 1828, where the spent activated carbon made from animal bones in sugar refineries was burned for regeneration (Taft, 1969). This method of regeneration aims to reestablish the adsorptive capacity without changing the surface of the AC (Sheintuch and Matatov-Meytal, 1999). Throughout many years, several methods of regeneration have been discovered. These methods are categorized under desorption and decomposition. Desorption is called thermal regeneration where, it is induced by increasing temperature or extractive regeneration (Harriott and Cheng, 1988; Tamon *et al.*, 1990).

Thermal regeneration: Thermal desorption is drying process and high temperature reactive treatment (700-1000°C) in the presence of inert gasses or of restricted quantities of oxidizing gasses (Harriott and Cheng, 1988). However, due to the high temperature during regeneration, the adsorption capacity and surface area shows a continuous decrease of 5-15% per cycle. Thus, indicating that at high temperature, it weakens the carbon structure and clogs the smaller pores.

Extractive regeneration: The methods in extractive regeneration are supercritical fluid extraction and surfactant-enhanced regeneration. Supercritical fluid extraction shows an improvement in mass-transfer properties over liquid solvent extraction. However, with supercritical fluid extraction using CO_2, regeneration of AC completely with organics could not be achieved. Further, it requires a large amount of CO_2. On the other hand, surfactant-enhanced regeneration process, the spent AC is flushed with concentrate surfactant solution (Bhummasobhana *et al.*, 1996). Nevertheless, the frequent usage of these regeneration techniques has been becoming more expensive and non-environmentally friendly. Because these methods are only transferring the contaminants in the AC from one place to another which requires repetitive treatment (Sheintuch and Matatov-Meytal, 1999).

Reactive regeneration: The method in reactive regeneration terminates the adsorbed organics by chemical, microbial or electrochemical processes. These methods may involve thorough mineralization of the adsorbed adsorbates, conversion of complex molecules into simple compounds and the transformation of hazardous materials to a compound where it is more desorbable, water-soluble or bio-degradable (Sheintuch and Matatov-Meytal, 1999).

CONCLUSION

Adsorptive-denitrogenation is one of the best methods to be used in removing NCCs from fuel, as the adsorption is inexpensive and does not require the usage of expensive hydrogen, high temperature, as well as high pressure. To successfully remove the nitrogen in the fuel, the nature (pH) of the nitrogen must be known. Once this is known, preparation of the adsorbents can be made, that is to impregnate and activate it with a suitable type of chemical. Other than manipulating the pH of the activated carbon, the specific pore surface area is also important as it contributes to adsorptive capacity. The optimum surface area can be acquired with the right activation temperature.

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