Journal of Materials and
Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 5, Page 1847-1852

http://www.jmaterenvironsci.com/

Morphological and Thermal Characterization of coking formed inside petrochemical distillation columns

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Received 19May2016,
Revised 22Feb 2017,
Accepted 28Feb 2017

Keywords

- ✓ Characterization;
- ✓ Thermal;
- ✓ Morphological;
- ✓ Coking;
- ✓ Distillation columns

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Abstract

This paper presents the results of the characterization of coking formed inside petrochemical distillation columns was investigated by using CHNOS, TG–DTG, FTIR, and XRD techniques. TG–DTG study revealed the decomposition of volatile species and FTIR analysis identified the presence of C–O, C–O–C, and some alkyl species on the surface of the coking. XRD results indicated that the coking studied is amorphous in nature; this reveals the presence of a fully amorphous carbon. The results showed that temperature is the cause of coking formation and probably even catalysts. As a result, the properties of the coking, such as the high carbon content, low volatile matter content and increased sulphur content can be used as anode grade type coking or low sulfur.

1. Introduction

In petrochemical industry, distillation columns are one of the main components, and the efficiency of the industrial plant relies on the ability of these columns to obtain the required separation of the mixture and the correct purity [1-3].

Coking is a grey to the black solid carbonaceous residue that is produced from petroleum during thermal processing, inside packed beds columns; characterized by having a high carbon content (95%+ by weight) and insoluble in organic solvents [4]. The applications of thermo-analytical techniques in the study and characterization of petroleum and petroleum products are gaining growing field of interest for analysts, petroleum chemists and engineers [5]. The chemical composition of petroleum coke is determined by the composition of the feed stocks used in the coking process, which to their turn depend on the composition of the crude oil and refinery processing from which the feedstock is derived. Cokes produced from feed stocks high in asphaltenes will contain higher concentrations of sulphur and metals than cokes produced from high aromatic feed stocks, because the asphaltenes contain a disproportionate fraction of those heteroatoms [6]. The different types of variables that determine the quality of coking; such as: density, metal and sulphur content, electrical resistivity. However, the Knowledge of structure parameters permits to determinate the characterization and usage of petroleum coke [7].

The coking contains sulfur with a percentage that depends on. But this percentage varies from under 0.5% to over 10%.the organic sulfur exists in the majority on coke, it is bound to the carbon matrix of the coke [8]. But the inorganic sulfur mixes found on the coke surface or in pores of coke bound by capillary condensation, adsorption or chemisorption [9].

Therefore, the chemical composition according to the type of polyaromatic carbon in coked feed stocks, together with the quantification of metallic heteroatoms, such as Nickel, Vanadium and Calcium (as recently reported), allowed morphology prediction in formed cokes within the collector drum. This conclusion broadens the metallic interval that, in general terms, is restricted to the Nickel/Vanadium couple, commonly used in morphology orientation and prediction in the cokes obtained during the coking reactions [10-11].

Metals, mainly vanadium and nickel, occur as metal chelates or porphyrins in the asphaltene fraction some metals are intercalated in the coke structure and are not chemically bonded, so they become part of the ash and particulates [12].

In Furfural solvent production unit in major Moroccan refinery which has experienced a serious problem of the coking formation inside packed beds columns. Because of this problem the unit was operating at only 10% of its nominal capacity. The aim of the present paper is to evaluate the physical-chemical characteristics of coking as a challenging issue in the petrochemical industry. Usual methods for characterization of materials were used, such as: Elemental analyzer CHNS, density, XRF fluorescence for chemical analysis; XRD for mineralogical characterization, thermal methods, such as DTA/TG analysis.

2. Experimental details

2.1. Sample

Coking is obtained from the Moroccan refinery (figure.1), which has mainly experienced a serious problem of the coking formation inside packed beds columns.

Figure 1: Sample of coking

2.1. *Carbon, Hydrogen, Sulphur and Nitrogen Analysis (CHNS)*

The use elemental CHNS analyzer provides the successful determination of C, H, and N in substances of any elemental composition and structure [13].

A CHNOS Element Analyzer (PerkinElmer 2400 Series II CHNS/O Elemental Analysis) was used to determine the weight percent of carbon, hydrogen, nitrogen, sulfur and oxygen ofcoking sample. The sample (2.30 mg) was used in a tin boat assortment for percentage composition of C, H, N and S.

2.2. *Chemical analysis*

Portable X-Ray Fluorescence (PXRF) has seen widespread use in the last 5 years, as it promises non-destructive inexpensive analysis of large numbers of samples both in the lab and in the field [14-15].

Metals also have been measured in coke sample coking sample by X-ray.The portable XRF analyzer to BRUKER brand with a maximum voltage of 45 or 50kV, the maximum intensity of100 or 200µA.And Power: 2W max) was used to determine the chemical composition of the spent prebaked aluminium carbon anode types investigated.

2.3. *Thermogravimetric Analysis (TGA)*

Thermogravimetric analysis (TGA) has been used in the evaluation of the thermal stability of materials [16], this analysis using only a combustion step with oxygen were used to characterize carbonaceous products. TG/DTG analysis of the coking sample was performed using labsys TM, instrument, SETARAM TG/DTA. The purpose of TGA is to understand the devolatilization characteristics of the coking with temperature. Therefore, 14,2mg of sample has been, taken and studied the devolatilization characteristics from 10 to 20°C at the rate of 1000°C/min.

2.*4. Characterization of the coking by infrared spectroscopy (IR)*

Infrared spectroscopy belongs to the group of molecular vibrational spectroscopies hich are molecule-specific and give direct information about the functional groups, their kind, interactions and orientations. Its sampling requirements allow the gain of information from solids, liquids and gases, and in particular from solid surfaces. Even if historically IR has been mostly used for qualitative analysis, to obtain structural information, nowadays instrumental evolution makes non-destructive and quantitative analysis possible, with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in metal sorption [17].This technique allows the identification of functional groups present in the solid surface. We set the goal in this study to examine the coking. We used a Fourier transform spectrometer (FT-IR) kind JASCO FT / IR-4600. The samples were pelleted with anhydrous KBr at 0.001 g of the sample for 0.15 g of KBr and examined in a field of vibration of from 4000-400 cm-1.

2.5 *XRD analysis*

Powder X-ray diffraction (XRD) was used to determine the crystallographic structure of the sample [18]. X'Pert3 diffractometer Powder (PW3064) X-ray diffractometer was used to record scattering intensities of samples by using monochromatic Copper (Kα(Å)=1,541874 et Kβ (Å)= 1,392250 radiation (45kV, 40 mA) as the X-ray source.

3. Results and discussion

3.1. Analytical Characterization

The physical-chemical properties of coking are determined using CHNOS Analyzer and the portable X-ray fluorescence (PXRF) analysis. Metals also have been measured are shown in Table 1.

Table 1: Characteristics and physical-chemical properties of coking using CHNOS and XRF methods

Methods	Characteristics	Coking
CHNOS	Carbon %	72.71
	Hydrogen %	3.48
	Nitrogen %	0.20
	Sulphur %	1.59
XRF measurements	Metals, mg.kg-1	
	Mg	10050 ± 1612
	Al	2755 ± 186.2
	K	3860 ± 111.5
	Ca	1680 ± 72
	Fe	1395 ± 45.5
	Cr	17 ± 8
	Mn	171 ± 6
	Ni	58 ± 4
	Cu	29 ± 4.5
	Zn	24 ± 2
	Sr	8 ± 2

Table 1 summarizes analysis results of coking; this coking sample has a high content of carbon (72.71%), sulphur, magnesium, potassium, calcium and iron with low content of manganese, nickel, copper, zinc, chromium and Strontium. We haven't possibility to measure of O2 by CHNOS. The relatively high sulphur content in coke (1.59%) is a consequence of high sulphur content in the feedstock (1.75 - 2.00%) [19].

The formation of heavy metals in the coking was also reported of the catalysts presence. On account of its high carbon content, low volatility, and ash content, petroleum coke is these days considered as a good precursor for preparing high surface area activated carbon [20].

3.2. Thermogravimetric Analysis

Fig. 2 shows the TG and DTG profiles of coking sample. The coking sample exhibited a slight weight loss from 50 to 350 °C and an about 20% weight loss starting from about 400 to 800 °C. The slight weight loss was attributed to the release of the moisture and the later loss could be due to the decompositions of volatiles. The DTG profile of coking sample further revealed that the volatiles decomposition started at about 420°C and lasted a wide temperature range with a broad wide temperature at about 780°C. The wide temperature range may be due to the overlap of thermal decomposition of multi-unstable species on the surface of the sample, implying the presence of various structures in the coking sample.

The phenomena observed during the course of the treatment include a significant amount of weight loss along with the removal of sulphur [9].

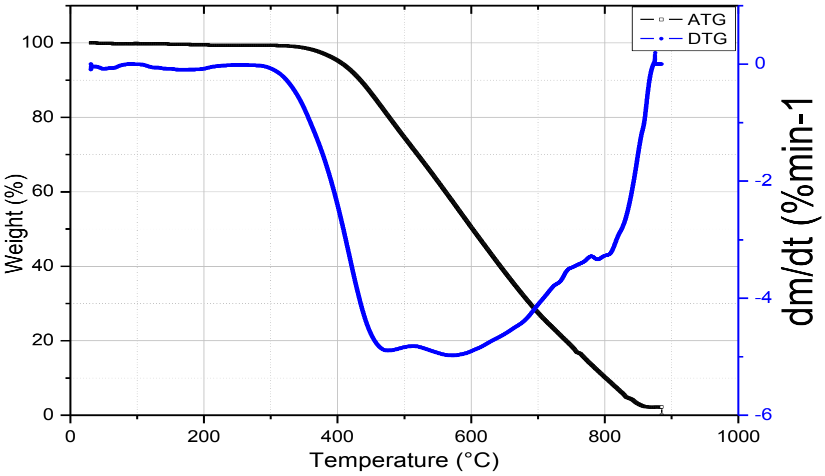

Figure 2: TG and DTG curves for the coking sample

Fig. 3illustratestheDTG and DSC profiles of coking sample. The wide endothermic band around 350–700°C consisted of the release of volatiles, combustion of the coke char and the combustion of coking volatiles. Finally, close to 750°C, there is a small endothermic indicating the starting of the combustion of fixed carbon and minerals decomposition.

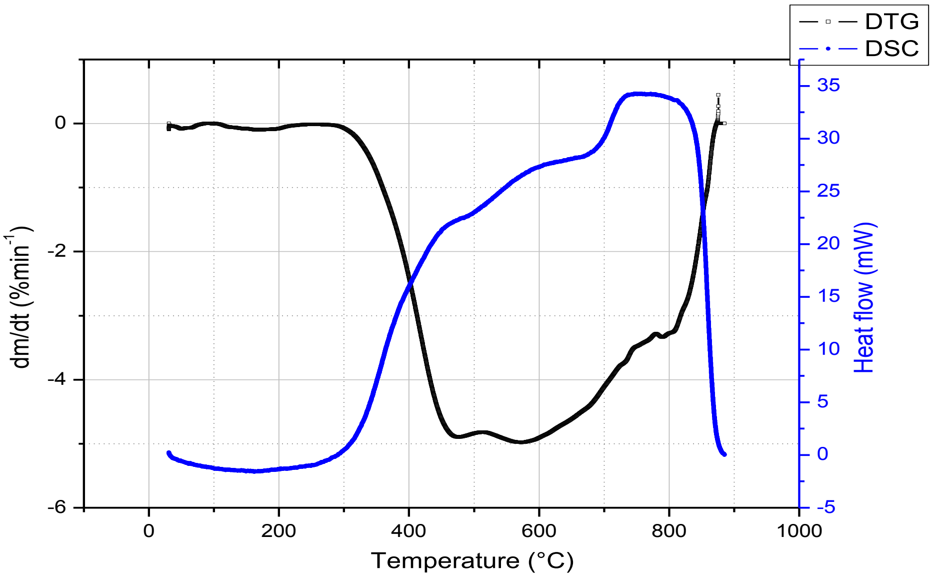

Figure 3: DTG and DSC curves for the coking sample

The results obtained indicate that the process of desulphurization may be divided into several steps: in the first step of heat treatment (about 500 °C) the biggest part of the separated sulphur takes place in the form of gases (H2S and RSH), from desorption of chemisorbed sulphur in coke pores or in the coke surface. This is the inorganic form of sulphur in coke samples. The partial decomposition of organic sulphur also takes place; this is the organic sulphur compounds bound in some chain [4].

3.3. *FTIR Spectroscopy*

Fig. 4 shows the FTIR spectra of the coking sample. The coking can be recognized by the bands at 3124.35 cm-1 (corresponding to an aromatic C-H stretching vibration) and at 2914.88 cm-1 (stretching and deformation vibration: alyphatic groups CH, CH2, CH3). As well as the frequency bands at 2353.69-2112.64 cm -1 (stretching vibrations) attributed to C≡N and C≡C groups. It can also be noted that, basically, the functionalities are related to the existence of stretching vibration C=O carbonyl groups (1721.1- 1669.79cm-1), and ether C-O-C groups (1145.51-1013.41 cm-1).The frequency bands at 1565.92 cm-1 can be assigned to the bonds of stretching vibration of nitro aromatic C-NO2. On the aliphatic side, the spectra consist of a pattern of absorption bands (region between 1463.74 and 1300- cm-1) corresponding to stretching vibrations of saturated groups (C-H, -CH2- and -CH3). Finally, the band at 745 cm-1 corresponding to deformation vibrations aromatic =C-H bonds in the aromatic rings. These surface functional groups can serve as active sites where chemical transformations occur via surface reactions.

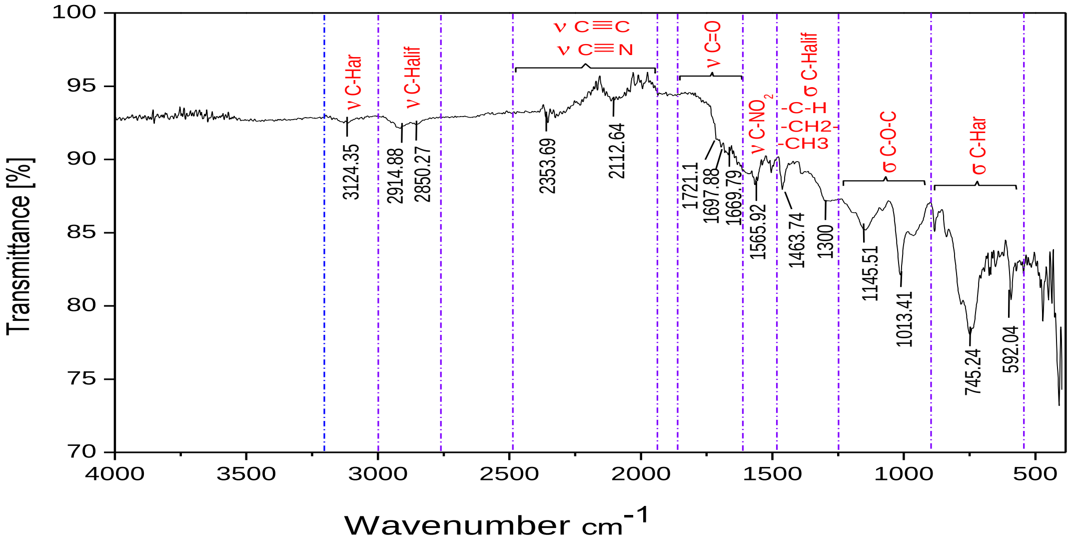

Figure 4: Infrared spectrum of coking

3.4 *XRD Analysis*

Figure 5 illustrates the powder X-ray diffraction (XRD) pattern of the coking sample. The XRD diffraction pattern of the coking sample (Figure 3) represents only one peak. This peak determines the coking sample is amorphous.So, the peak is broader; this reveals the presence of a fully amorphous carbon.

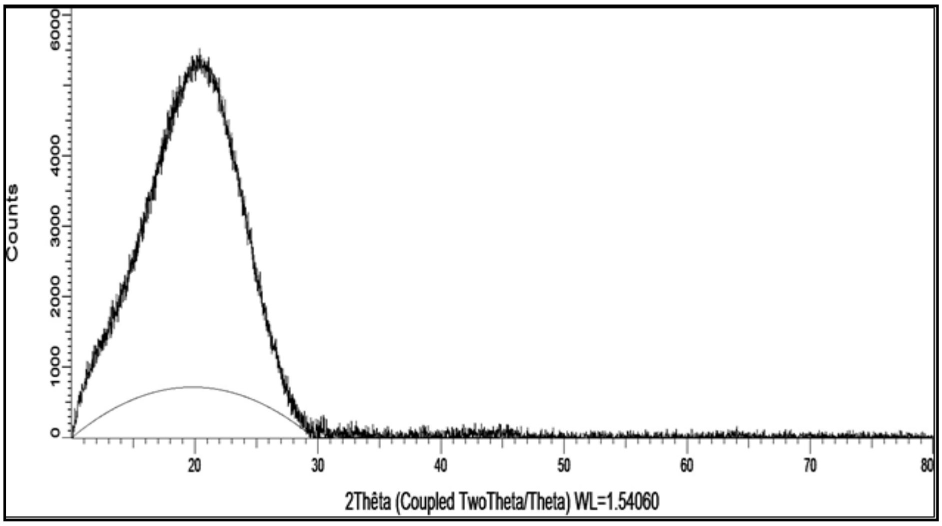

Figure 5: XRD diagram of coking

Conclusions

The present paper studied the characterization of coking formed inside petrochemical distillation columns in major Moroccan refinery. Coking formation, seriously affect product yield in packed columns and eventually leads to unnecessary and costly shutdowns. So, the characterization of such phenomenon at an early stage becomes a challenging issue for process engineers. The results showed that analyzed coking has a high carbon content, low volatile matter content and increased sulphur content. TG–DTG study revealed the decomposition of volatile species and FTIR analysis identified the presence of C–O, C–O–C, C-H and some alkyl groups on the surface of the coking. Increasing the coking temperature decreased noticeably the amount of these surface species. XRD results indicated that the coke studied is amorphous in nature; this reveals the presence of a fully amorphous carbon. From the characterization we have done to coking, it has been found that temperature is the cause of formation and probably even catalysts. What we have discerned according to fluorescence X.

As a result, the properties of the coking, such as the high carbon content, low volatile matter content and increased sulphur content can be used as anode grade type coking or low sulfur fuel.

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(2017) ; http://www.jmaterenvironsci.com