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Determination of the calorific value of syrian delayed petroleum coke

Abstract

The calorific value is a significant indicator of the quality of coke when used as a fuel. It is often used for evaluating the effectiveness of treatment and other beneficiation processes and for research purposes. In the present work, the calorific value of samples of the basic types of Syrian petroleum coke was measured and calculated using empirical formulae and the results were compared. Significant differences were observed in the calorific values of the five types of the Syrian petroleum coke considered. It is concluded that further study of these and other types is merited for better and more economical utilization of the coke. A significant correlation was also observed between the calorific value and the volatile matter content of the coke.

Keywords: petroleum coke, calorific value

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Introduction

Delayed petcoke is petroleum coke produced by the delayed coking process, which is a semi-continuous batch process that can be carried out in one of three ways: ultimate, once-through or intermediate coking.[1] The first delayed coker was built by Standard Oil of Indiana at Whiting, Indiana in 1929. The number of cokers built before 1955 was, however, small.[2]

There are at least four basic types of delayed petcoke: needle coke, honeycomb coke, sponge coke and shot coke. Such different petcokes types have different microstructures due to differences in operating variables and the nature of feed stocks. The chemical composition of the feedstock is the controlling factor with regard to coke structure. Feed stocks with higher levels of nitrogen, sulphur, oxygen and asphaltenes and lower levels of aromaticity are the worst feed stocks which lead to the formation of shot cokes. As the feedstock changes to lower levels of hetero atoms and higher levels of aromaticity, so the coke type changes from shot coke, to clustered shot coke, to the porous sponge coke and continuous sponge coke with inclusions of high relative structural order, and ultimately to needle cokes.[3] Other factors affecting the type of coke produced include: Heater outlet temperature, Coking drum temperature, Recycle rate and Operating pressure.

Syrian delayed coke

Syrian delayed coke is coke produced by the delayed coking unit at the Homs Oil Refinery. This unit was designed and built during the late sixties of last century for the purpose of maximizing gasoline and distillate yields using a feedstock of residue materials. In this unit, heavy residue materials are coked at a temperature of 760 K and a pressure in the range 1.4-1.6 bars. The crude oil used is a blend of two crude oil varieties, with the blending ratio varying at different times. The Petcoke produced is considered merely as a by-product of little commercial value. This is mainly because of its high sulphur content and the high percentage of fines produced.

Calorific value

The calorific value (CV) or Heat of combustion is a measure of the heat liberated as a result of the complete combustion of the fuel. Customarily, the basic calorific value for petroleum coke and other solid fuels is the gross calorific value, or higher heating value, at constant volume (GCV). This is a measure of the heat liberated as a result of the complete combustion of a unit quantity, weight or volume, of the fuel when all products of the combustion are cooled down to the temperature before the combustion and the water vapour formed during combustion is condensed. As this combustion water vapour is normally discharged as vapour and not condensed, a lower heating value, or a net calorific value (NCV), is sometimes quoted. This is obtained by subtracting the latent heat of vaporization of the water vapour formed by the combustion from the gross calorific value. As a result of the low contents of both moisture and hydrogen in petcoke, the difference between the gross and net calorific values is generally less and seldom greater than about 3% of the gross value.

For the measurement of the calorific value of petcoke, the adiabatic bomb calorimeter method may be used (ASTM D-2025, ASTM D-5865). In another test method that is suitable for coke (ASTM D-3523), the coke sample is supported on surgical gauze and placed in a heated chamber that is open to air at the top. The temperature of this sample is compared with that of an equal reference quantity of surgical gauze contained in an identical chamber. Tests may be conducted for durations of 4-72 h or longer.

Much work has been done on measurements of the calorific value of coke, where the calorific value was found to vary greatly, not only with such properties as volatile matter and moisture content, but also, and more importantly with the carbon and hydrogen content of the coke samples. Volatile matter can be used in estimating the calorific value of coke. Some of the equations proposed originally for coal, but which could also be applied to coke are the Maydel and Schuster equations:

$$GCV = 37,414 - \frac{19,102}{34.83 - VM} \qquad \text{(Maydel)}$$

$$GCV = 33,600 + VM\left(294 - 6.93\,VM\right) \qquad \text{(Schuster)}$$

Where VM represents the volatile matter content of coke

In test method ASTM D-6446, the net calorific value is calculated from the density and sulphur and hydrogen contents. A number of empirical formulae are also available in the literature for the calculation of the calorific value of coke based on the ultimate analysis of the fuel.

These are generalized equations that may be used for all types of liquid or solid fuels.

$$GCV = 351\,C + 1163\,H + 105\,(S-O) \quad (1)$$

$$NCV = 351\,C + 941\,H + 105\,(S-O) \quad (2)$$

The Dulong equation is a further equation that may be used to calculate the calorific vaue of coal. This equatin was derived based on the assumption that each element in coal contributes to the its overall calorific value an amount equal to what it would contribute if it were in a mixture of elements and not chemicalluy combimed with other elemnets as in fact it is.

This equation is quite similar to the above equations 1 and 2 but with slightly different constants:

$$GCV = 339.4\,C + 1447.3\,(H - 0.125\,O) + 105\,S$$

$$NCV = 340.2\,C + 1218\,(H - 0.125\,O) + 105\,S$$

According to Cragoe,[4] the density or specific gravity may also be used for the calculation of the calorific value of petroleum products in general. The value obtained may have to be corrected, however, if the petroleum product contains significant amounts of moisture, ash or sulphur.

$$GCV_{uncorrected} = a - bd^{2} \quad (3)$$

Corrected

$$GCV = GCV_{uncorrected} - 0.01\,GCV_{uncorrected}\,(M + A + S) - 94.2\,S \quad (4)$$

a and b are constants (a = 51920, b = 8792). M, A and S are the weight percents of moisture, ash and sulphur respectively. For petroleum coke, the real specific density has to be used in the calculation of the calorific value, as this better represents the density of the coke. The real or true density of petcoke (DR10–20) is the density of 10-20 Tyler (0.83–1.65 mm) sample measured by The pycnometer.

Finally, in the Grummel-Davies equation, it was assumed that the calorific value correlates with the amount of air required for complete combustion.

$$GCV = (15.267\,H + 990.8)\left[0.33\,C + H - 0.125\,(O - S)\right]$$

The calorific value is often used for evaluating the effectiveness of treatment and other beneficiation processes and for research purposes. It is also a significant indicator of the quality of coke when used as a fuel. Fuel grade petcoke represents roughly 80 percent of worldwide petcoke production. It has in general a high calorific value (35 MJ/kg) compared to coal which has a calorific value that varies between 29 MJ/kg for bituminous coal to about 8 MJ/kg for lignite and brown coal. Petcoke also produces virtually no ash when burned. Furthermore, the low price and increased production of petroleum coke from high-sulphur feed stocks give a powerful economic stimulus to its use as an alternative fuel for power generation and in cement kilns and blast furnaces.

Petcoke may have to be upgraded before being used as a fuel. In particular petcoke is normally calcined and desulphurised. The calcination of coke is a high-temperature (>1000°C) pyrolysis treatment of green coke in which moisture and volatile matter (hydrogen, methane and tar) are removed. Desulphurization of petroleum coke and the reduction of its sulphur content to an acceptable level or eliminating it altogether is becoming a necessary process, in particular with the ever-tightening restrictions on sulphur oxides emissions for environmental considerations.[5] Upgrading and treatment of coke, however, may adversely affect its calorific value. For example, the calorific value of coke was found to drop as a result of hydrodesulphurization from 35.1×10^3 KJ/Kg to 34.2×10^3 KJ/Kg.[6]

Experimental work

For the present work samples of Syrian coke were taken from the coke heaps stored to the west of the refinery. These samples were classified and divided into three basic types, namely shot coke, sponge coke and fines. The shot coke samples were further subdivided into regular shot coke and clustered shot coke. Similarly, the sponge coke samples were subdivided into porous sponge coke and continuous sponge coke.

Significant differences are expected in the properties of the five different types of the Syrian petroleum coke considered, particularly ash and volatile matter contents with resulting significant effects on their calorific values.[7]

The coke samples were first crushed so that 95% of the coke passed through a 4-mm sieve. The samples were weighed and spread on a drying floor to a depth of 8 mm and left to dry until the loss in weight of the total samples was not more than 0.1% per hour. After the determination of the moisture content (As-received basis) the coke samples were pulverized to pass a 250-µm sieve. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods. For the calorific value determination, the adiabatic bomb calorimeter method was used (ASTM D 2025), in which a weighed sample is burnt completely in oxygen under controlled conditions. The calorific value is computed from temperature observations made before, during and after combustion, making proper allowances for heat contribution by acid formation and other corrections.

Proximate and ultimate analysis

Typical Proximate analyses for the Syrian green coke are given in Table 1. Typical analyses results for the Syrian green petcoke as obtained by ultimate analysis is given in Table 3. Syrian coke, as compared to other types of coke, has a lower than average carbon content and a higher content of hydrogen, nitrogen and oxygen. Whereas green coke is normally characterized by a high C/H ratio (>20), the value obtained for Syrian petcoke is less than 20 for all coke types considered. A possible reason for this could be found in the manner of storage of the Syrian coke. The Syrian coke is stored in a hot, windy and often humid environment. Under such conditions, spontaneous combustion is likely to occur with a consequent reduction of carbon content. The coke tends to oxidize or "cure" by adsorbing oxygen at temperatures below 200°C. The stored coke is also able to absorb oxygen for considerable lengths of time and green coke piles tend to generate considerable temperatures; typically 185-200°C in the centre of a 300-ton pile. Both factors, time and temperature, tend to increase the amount of oxygen adsorption. Such additions of oxygen tend to promote cross-linking between the graphitoid structures irreversibly decreasing the anisotropy of the calcined coke.[8]

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Table 1 Proximate Analysis of Syrian petcoke, air-dried basis

Property	Fines	Shot	Clustered	Porous	Continuous
Gross Calorific Value kJ/kg	34.9×10^3	34.7×10^3	34.3×10^3	34.8×10^3	35.1×10^3
Nett Calorific Value kJ/kg	33.8×10^3	33.7×10^3	33.3×10^3	33.8×10^3	34.0×10^3
VM (wt %)	14.7	9.9	9.8	12.5	15
Moisture (wt %)	0.3	0.2	0.4	0.3	0.5
Ash (wt %)	0.7	0.2	0.1	0.2	0.3
Fixed Carbon(wt %)	84.3	89.7	89.7	87	84.2
Sulphur (wt %)	7.9	7.9	8	7.7	7.7
Real density g/cm^3	1.38	1.4	1.37	1.4	1.39

The gross calorific value (GCV) for the different types of Syrian coke varied between 34.3×10^3 and 35.1×10^3 kJ/kg, with an average value of 34.8×10^3 kJ/kg (Table 1). The difference between the maximum and minimum values amounted to 2.3% of the average value. Similar variation was also observed for the net calorific value (NCV) which varied between 33.3×10^3 and 34.0×10^3 kJ/kg, with an average value of 33.7×10^3 kJ/kg (Table 1). Direct correlation was observed between the CV and volatile matter content (VM) which clearly indicates the significant contribution of the volatile matter content of the coke to its overall calorific value Figure 1.

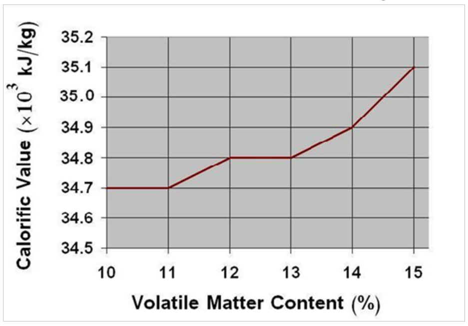

Figure 1 Calorific value Vs volatile matter content of Syrian Petroleum coke.

Calculation of the calorific value

The calorific value was computed using the generalized equations 1 and 2. Comparison between the calculated and measured values of the calorific value for both GCV and NCV is given in Table 2, where the differences between the measured and calculated GCV values varied between 0.3×10^3 and 0.6×10^3 kJ/kg, i.e. less than 2%.

Similar differences were also obtained between the measured calorific values and the values calculated using equations 3 and 4 (Table 3). The difference in this case varied between 0.0 10^3 and 1.1×10^3 for the uncorrected values and 0.1×10^3 and 0.6×10^3 kJ/kg for the corrected values. This clearly indicates that density measurements may be used for the estimation of the calorific value of petcoke Table 4.

When the Maydel equation was used for the calculation of the calorific value, an average value of 36.6×10^3 kJ/kg was obtained, which is rather higher than expected. Similar higher values were also obtained using the Schuster, Dulong and Grummel-Davies equations (Table 5). This indicates that using these equations which were originally proposed for coal are not the best equations to use with Syrian petroleum coke (Table 6).

Table 2 Comparison between measured and calculated calorific values (Eq. 1 & 2)

Type of coke	Gross calorific Value kJ/kg		Nett calorific Value kJ/kg	
	calculated	measured	calculated	measured
Fines	34.3×10^3	34.9×10^3	33.2×10^3	33.8×10^3
Shot	34.1×10^3	34.7×10^3	33.1×10^3	33.7×10^3
Clustered	33.9×10^3	34.3×10^3	33.0×10^3	33.3×10^3
Porous	34.5×10^3	34.8×10^3	33.5×10^3	33.8×10^3
Continuous	34.8×10^3	35.1×10^3	33.7×10^3	34.0×10^3

Table 3 Comparison between measured and calculated calorific values (Eq. 3 & 4)

Type of coke	Measured gross calorific value kJ/kg	Calculated calorific Value kJ/kg	
		uncorrected	corrected
Fines	34.9×10^3	35.2×10^3	34.8×10^3
Shot	34.7×10^3	34.7×10^3	34.3×10^3
Clustered	34.3×10^3	35.4×10^3	35.0×10^3
Porous	34.8×10^3	34.7×10^3	34.3×10^3
Continuous	35.1×10^3	34.9×10^3	34.5×10^3

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Table 4 Ultimate Analysis of Syrian petcoke, Dry, ash-free basis

Property	Fines	Shot	Porous	Continuous
Carbon	82.9	84.7	84.9	84.4
Hydrogen	4.9	4.3	4.6	5.1
Nitrogen	1.2	1.1	1.1	1.2
Oxygen	3	2	1.7	1.5
Sulphur	8	7.9	7.7	7.8
C/H (wt.)	16.9	19.7	18.5	16.5

Table 5 Comparison between measured and calculated calorific values (Using Maydel, Schuster, Dulong and Grummel-Davies equations)

Type of coke	Measured gross calorific value kJ/kg	Calculated Calorific value kJ/kg			
		maydel	schuster	Dulong	Grummel-Davies
Fines	34.9×10^3	36.5×10^3	36.4×10^3	35.5×10^3	34.7×10^3
Shot	34.7×10^3	36.6×10^3	35.8×10^3	35.4×10^3	34.8×10^3
Clustered	34.3×10^3	36.6×10^3	35.8×10^3	35.4×10^3	34.8×10^3
Porous	34.8×10^3	36.6×10^3	36.2×10^3	36.0×10^3	35.4×10^3
Continuous	35.1×10^3	36.4×10^3	36.5×10^3	36.6×10^3	36.1×10^3

Table 6 Effect of the thermal treatment temperature on the calorific value of Syrian petcoke

Temperature K	Calorific value×103 kJ/kg				
	Porous sponge coke	Continuous sponge coke	Regular shot coke	Clustered shot coke	Coke fines
300	34.8	35.1	34.7	34.3	34.9
500	35.1	35.1	34.7	34.2	35.1
775	34.7	34.9	34.5	34.5	34.5
875	34.3	34.9	34.8	33.8	34
975	33.3	32.4	32.4	32.4	32.8
1075	32.4	32.4	32.3	32.3	32.3
1175	31.9	31.4	31.9	32	31.7
1450	31.1	31.2	31.8	31.6	30.9
1550	32	32.2	31.8	31.9	32.4
1650	30.6	32.4	31.8	31.9	32
1700	32.1	31.2	32	32.5	32.1

Calorific Value of upgrade petcoke

With the increasing value and importance of delayed coke, many studies have been undertaken for the purpose of investigating different processes for upgrading the coke such as activating the coke,[9–11] reducing its sulphur content and/or increasing its real density. Such upgrading processes tend on the whole to have some significant effect on its calorific value.

Thermal treatment of Syrian petcoke was found to be the most appropriate desulphurization process, in which the coke was heated under atmospheric pressure in an inert atmosphere to a specified temperature and then kept at that temperature for a specified period of time.[12,13–16] This process usually involves primarily thermal decomposition and dehydrogenation, but polymerization and isomerisation may also take place to some extent. In most cases, the calorific value of the coke decreased with increased temperature of the thermal treatment (Table 4), although a slight increase in the calorific value was observed during certain stages of the thermal treatment. This increase was a result of the removal of both moisture and sulphur from the coke Figure 2.[17]

Solvent extraction is not generally an effective desulphurization process for high-sulphur petroleum coke. However, pre-oxidation of the Syrian petroleum coke at a moderate temperature (600 K) rendered the coke more amenable to the solvent extraction treatment. As a result of pre-oxidation, the calorific value was reduced by about 14%.[18] Pre-oxidation of petroleum coke at a moderate temperature

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(600 K) for a short period of time (15 minutes) lead to a reduction of the calorific value of Syrian petcoke by about 14%.[18]

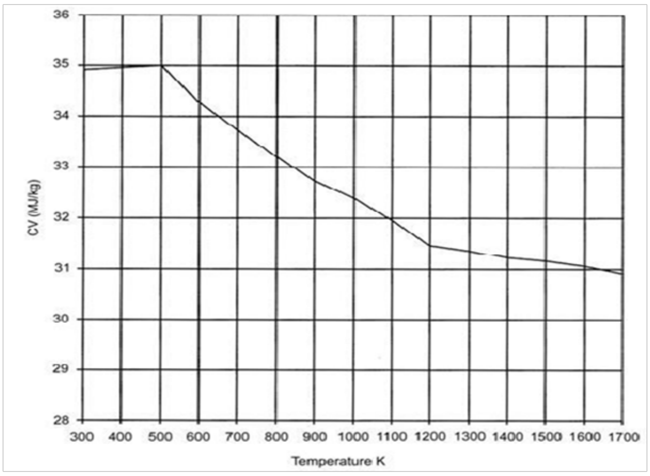

Figure 2 Variation of calorific value (CV) with heat treatment temperature.

Conclusion

The results of the measurements and calculations carried out indicate that different petcoke types differ in their calorific values, and that these differences are significantly related to the volatile contents of the coke. The differences between the measured and the calculated values using available empirical formulae are insignificant on the whole amounting to less than 2%, which indicates clearly the feasibility of using such formulae in the absence of laboratory facilities for the determination of the calorific value.

Nomenclature

A Weight percent of ash

C Weight percent of carbon

CV Calorific value

DR10-20 The real or true density of petcoke. This is the density of 10-20 Tyler (0.83-1.65 mm) sample measured by He pycnometer

GCV Gross calorific value, or higher heating value, at constant volume

H Weight percent of hydrogen

M Weight percent of moisture

NCV Lower heating value or net calorific value

O Weight percent of oxygen

S Weight percent of sulphur

VM Volatile matter content of coke

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None.

Conflict of interest

The author declares no conflict of interest.

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