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Composition of Natural Gas and Mazout Fuels in Cement Industries in Relation to Their Calorific Values and Environmental Effect

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ABSTRACT: Two gas samples and two mazout samples which used as fuels in Cement Companies were collected. These studied fuel samples were analyzed for compositional analysis and calculation of their calorific values via capillary gas chromatography connected with TCD and FID according to standard methods. These fuels need to have an appropriate chemical energy content which depends on the type of components and their organic content. There are a number of factors that promote the use of fuels in cement kilns. Of these factors, the most notable are: the high temperatures developed, the appropriate kiln length, the long period of time the fuel stays inside the kiln and the alkaline environment inside the kiln. The fuels used should fall within the extreme values of parameters such as: minimum heating value, maximum humidity content, and maximum content of heavy and toxic metals. It has been found that the net and gross heat values of the used natural gas fuel are 1014 Btu/ft^3 and 1032 Btu/ft^3 respectively. Mazout fuel exhibits net and gross heat values between 40313 and 43565 kJ/kg, these date reflect the preferred natural gases as fuels not only due to the higher calorific values but also it is friendly environment.

KEY WORDS: Gas samples**,** Mazout samples**,** Cement company, Compositional analysis, Calorific values**,** Net and gross heat values.

I. INTRODUCTION

Cement kilns are used for the pyroprocessing stage of manufacture of Portland and other types of hydraulic cement, in which calcium carbonate reacts with silica-bearing minerals to form a mixture of calcium silicates. Over a billion tonnes of cement are made per year, and cement kilns are the heart of this production process. Cement manufacturing requires very large amounts of energy and used a variety of energy inputs. Among the most common types of fuels are fuel oils, coal, petroleum coke, mazout and natural gas [1]. In addition, in all three countries, certain hazardous – such as used lubricants and contaminated soils – and non-hazardous wastes – such as scrap tires -- can be burned as fuel in the rotary kilns [2-6]. These decisions in turn have environmental consequences in terms of the emissions of toxics and other atmospheric contaminants, global greenhouse gases and the generation of large quantities of cement kiln dust (CKD) waste. In favorable circumstances, high-rank bituminous coal can produce a flame at 2050 °C. Natural gas can only produce a flame of, at best 1950 °C, and this is also less luminous but it accompanied with less pollution, mazout is a heavy fossil fuel that is currently being used in the clinker production process at cement Plant.

The most important uses of cement are as an ingredient in the production of mortar in masonry, and of concrete, a combination of cement and an aggregate to form a strong building material. Gas chromatography connected with thermal conductivity detector and flame ionization detector is the best analytical tool used for separating natural gas fuel. The high efficiency of separation depends on the selective column used (7-10) and the detector type (11). The compositional analysis (12) and calorific values (13) were achieved using standard methods.

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II. EXPRIMENTA

II.1 Sampling

It is a' waste of time, manpower, and money to make a highly accurate analysis and inaccurately collected sample, so the sampling is as important as the analysis itself. The greatest care must be exercised in obtaining a representative sample and these samples must be taken by personnel trained in sampling techniques. Two natural gas samples and two mazout samples were collected from cement industry by evacuated cylinder method according to API recommended practice for sampling petroleum reservoir fluids [14]. This method depends on purging method and filling a piston type cylinder. It has the advantage of making it easier to maintain the sample in single phase whilst sampling and in addition the sample does not come into contact with any other fluid that might give rise to contamination.

II.2 Sample quality checking (Sample validity checks)

The gas sample container was heated to the temperature at which the sample was collected and stabile for two hours with shaking to revalorize any liquid. With the cylinder in the vertical position the bottom valve was cracked carefully to check for liquids and then the opening pressure was determined. This pressure was equal to or slightly greater than the pressure at the time of sampling.

II.3 Gas chromatographic analysis

The analysis was performed using an Agilent 6890 plus HP gas chromatograph equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) under the following conditions: The instrument is fitted with three columns, the first is 13x molecular sieve to separate O_2, N_2 and Methane, the second is porapak to separate CO_2 and light gases, the third is OV 101 column to separate the remaining hydrocarbons. The analysis occurs under two programmed of temperatures, the first initial temperature 50 °C at 7 min initial time with 20 degree min-1 till reached to the first final temperature 120°C which heated with 10 degree min-1 till reached to second final temperature 240°c and final time 10 min. Helium was used as carrier gas for TCD with flow rate 25 ml min"} and Nitrogen was used as carrier gas for FID with flow rate 30 ml min-t. The injector temperature was 220 °C and both the detector temperatures were 300 ^{o}C. The instrument was connected with the board data handling system for computing the peak area and mol percent. The quantitative analysis was conducted by analyzing standard reference samples of natural gas containing CO_2 of mol percent ranging from 1 % to 100%.

III. RESULTS AND DISCUSSIONS

This paper examines issues related to the use of energy inputs in the manufacture of cement clinker. Energy use and in particular fuel use is a major price factor in the production of cement. Because of this, companies in all three countries have invested in energy efficiency measures, such as converting wet kilns to dry kilns, or to adding precalciners and predryers to their cement production process, a more efficient process in terms of fuel use. Air emissions are determined both by the type of fuel burned as well as the types of pollution control equipment used by cement manufacturers.

III.1. Compositional analysis of natural gas

The complete analysis of the major hydrocarbons in the two studied natural gas samples collected from Cement Company was given in Table 1. Considerable variations in the hydrocarbons distributions can be found in the studied gases. The natural gases contain hydrocarbons and non hydrocarbons, the hydrocarbons are methane, ethane, propane, butanes, pentanes and hexanes. The non hydrocarbons include nitrogen and carbon dioxide. There is no one chromatographic column and one detector can separate the all components present in natural gases, so, we use three different columns and two detectors in order to obtain complete analysis of the extracted natural gases.

The first column used is capillary column packed with silicon oil stationary phase coated on the surface of chromosorb WAW for separating the heavy hydrocarbons in natural gas, the second is molecular sieve capillary column for

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separating nitrogen and oxygen and the third packed column is Porapack-Q for separating methane, ethane and propane in addition to carbon dioxide. The first detector used is thermal conductivity detector for light paraffines and non hydrocarbons and the second one is flame ionization detector for heavy hydrocarbons. From these columns and detectors, the complete analysis of natural gas was shown in Fig. 1, the chromatogram contains the all hydrocarbons and non hydrocarbons present in natural gas. The mean percentage of methane in the two natural gases was given in Table 1 represents the highest value, the complete compositions of gases include low percentage of nitrogen and considerable amounts of carbon dioxide. Each gas contains paraffines up to hexanes. Ethane represents the second high percentages in natural gas samples after methane. These variations are reflected on the physical properties of the gases such as specific gravity molecular weight as given in Table 1. For example, the highest methane value is accompanied by the lowest values of density, gas gravity and molecular weight.

III.2. Calculation of heat values of natural gas

The calorific values of the studied natural gas fuels are given in Table 2. It has been found that both gross and net calorific values of the natural gases are 1014 and 914 Btu/ft^3 respectively for saturated gas and 1032 and 931 Btu/ft^3 respectively for dry gas calorific values depends on the composition and the percentages of hydrocarbons in natural gas. This difference may be due to two reasons the first is the high presence of water content in saturated gas on the expense of hydrocarbons corresponding to day gas, the second reason is the slightly higher percentage of non hydrocarbon components in saturated gas than day gas, these compounds have no heat values.

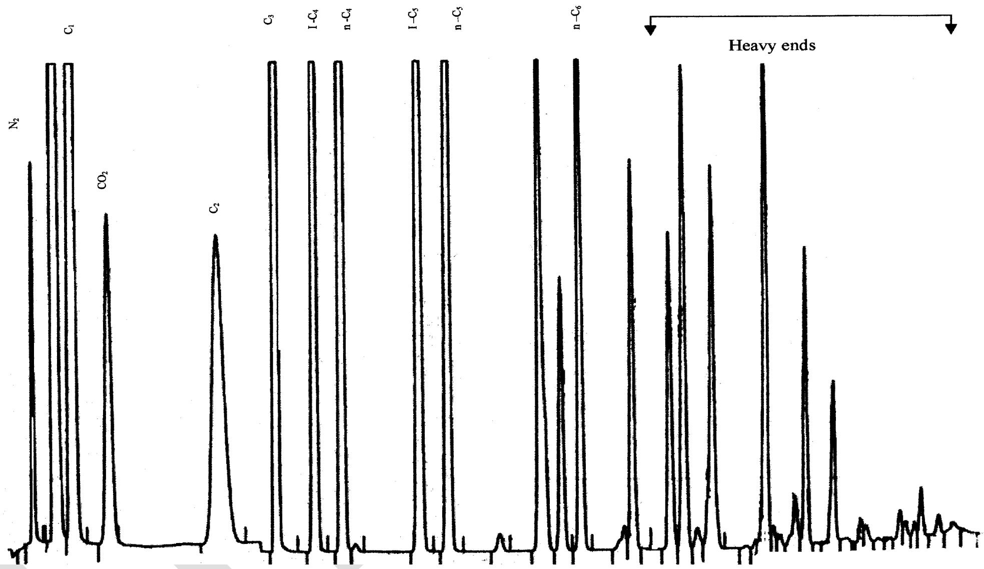

Figure 1. Chromatogram model of GC analysis of natural gas sample 1.

Table 1 gas chromatographic analysis of natural gases

Composition	Natural Gas 1		Natural Gas 2	
	Mol. %	Wt. %	Mol. %	Wt. %
Nitrogen	0.561	0.880	0.553	0.868
Methane	90.489	81.312	90.478	81.316
Carbon Dioxide	2.639	6.505	2.608	6.43
Ethane	5.652	9.519	5.706	9.612
Propane	0.552	1.363	0.549	1.356

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Iso-Butane	0.02	0.065	0.020	0.065
Normal-Butane	0.009	0.029	0.009	0.029
Iso-Pentane	0.036	0.145	0.035	0.141
Normal-Pentane	0.026	0.105	0.025	0.101
Hexanes	0.016	0.077	0.017	0.082
Total	100.000	100.000	100.000	100.000
Density gm/l @ NTP	0.7971		0.7969	
Average Molecular Weight	17.854		17.851	

The main observation on the hydrocarbons distributions may be that a considerable amount of non methane hydrocarbons are present in the majority of the studied gases. These are promising indications for these gases as primary materials for petrochemical processes, as well as, a valuable source for energy. From another point of view, the hydrocarbons distributions in the gases may contribute as gas fuels in engine motor.

III.3. Petroleum analysis of mazout samples

Mazout is a heavy, low quality fuel oil, used in generating plants and similar applications. In the west, furnaces that burn mazout are commonly called "waste oil" heaters or "waste oil" furnaces. Mazout product is typically used for larger boilers in producing steam since the BTU content is high. It is part of the products left over after gasoline and lighter components are evaporated from the crude oil.

Table 2. Calculation of heat values of natural gases

Calorific values	**Natural Gas 1**		**Natural Gas 2**	
	Saturated gas	Dry gas	Saturated gas	Dry gas
Relative Density(Air= 1.0000)	0.6175	0.6164	0.6174	0.6163
Gross Calorific Value, Btu/ft^3	1014.019	1032.037	1014.742	1032.773
Gross Calorific Value, Mj/m^3	37.781	38.453	37.808	38.480
Gross Calorific Value, Btu/lb.	21,936	21,936	21,956	21,956
Gross Calorific Value, Kj/Kg	51,023	51,023	51,070	51,070
Net Calorific Value, Btu/ft^3	914.788	931.043	915.451	931.718
Net Calorific Value, Mj/m^3	34.084	34.690	34.109	34.715
Net Calorific Value, Btu/lb.	19,789	19,789	19,807	19,807
Net Calorific Value, Kj/Kg	46,029	46,029	46,071	46,071

The main difference between the different types of Mazout is the content The most important consideration when grading mazout fuel is the sulfur content, which can mostly be affected by the source feedstock. of sulphur.

Table 3. Results of Mazout Samples

Experiment	**Method**	**Result of Mazout 1**	**Result of Mazout 2**
Density, @ 120 ^{o}C, g/ml Density, @ 15.56 ^{o}C, g/ml Specific Gravity API gravity @ 60 ^{o}F	ASTMD-1298	0.8850 0.9539 0.9548 16.69	0.8825 0.9515 0.9524 17.07
Kinematic viscosity, cSt, @ 50 ^{o}C	ASTM D-445	186.41	154.05
Kinematic viscosity, cSt, @ 80^{o}C	ASTM D-445	40.24	32.67

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Kinematic viscosity, cSt, @ 120°C	ASTM D-445	10.91	8.91
Flash point, °C	ASTMD-92	169	189
Pour point, °C	ASTM D-97	42	39
Water content, %	ASTMD-95	0.5	2
Carbon residue, wt %	ASTM D-189	9.84	8.83
Ash content, wt %	ASTM D-482	0.195	0.157
Asphalten content, wt %	IP-143	4.16	3.62
Nitogen content, wt %	ASTM D-3228	0.14	0.11
Total Sulphur, wt %	ASTM D-4294	1.25	1.22
Carbon, wt%	-	86.94	86.99
Hydrogen, wt%	-	10.68	10.71

The petroleum tests of the two studied mazout fuel samples are given in Table 3.
The petroleum tests are density, API gravity, kinematic viscosity, flash point, pour point, water content, carbon residue, ash content, asphalten content, nitogen content, total sulphur, carbon, wt%, hydrogen, wt% add both gross and net heating value kJ/kg.

Density at 15.56 °C and 120 °C and kinematic viscosity at 50 °C, 80 °C and 120 °C for mazout sample number 1 exhibits slightly higher values than that of mazout sample number 2 reflecting that mazout 1 one has higher molecular weight than mazout 2. This conclusion was matched with the result of API gravity of the two mazout samples which given in Table 3.

The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to help characterize the fire hazards of liquids. The flash point of mazout is the lowest temperature at which it can vaporize to form an ignitable mixture in air. The flash point of mazout sample 1 can vaporize to form an ignitable mixture in air at temperature 169 oC lower than that of mazout sample 2 which forms ignitable mixture in air at temperature 189 oC. Mazout sample 1 has pour point higher than that of mazout sample 2 reflecting that sample number 1 has paraffin content higher than sample 2. Mazout 1 exhibits high gross heating value corresponding to mazout 2 indicating sample 1 has high molecular weight and that it contains heavy hydrocarbons.

IV.CONCLOUSIONS

- Cement manufacturing is a key and growing industry in all three countries, and a major user of energy. Cement producers make decisions about the type of energy used to fuel the kilns where the cement clinker is produced.
- Energy use and in particular fuel use is a major price factor in the production of cement, natural gas and mazout fuels are preferred fuels compared with waste generation energy.
- Both gross and net calorific values of the saturated natural gases exhibit low values compared with dry natural gas due to its low percentage of hydrocarbons.
- Generally, Mazout product is typically used for larger boilers in producing steam since the BTU content is high. Mazout 1 has higher molecular weight than mazout 2 due to its high density, high pour point and matched with its high heat values.

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