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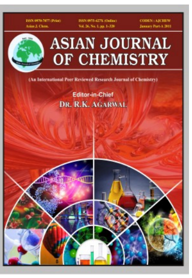

Gas Chromatographic Analysis of Automobile Gasoline and Lighter Gas Using Phenyl-Modified Aleppo Bentonite

ABDUL AZIZ RAMADAN*, SAAD ANTAKLI and MOHAMAD SUBHI SAMMANI

Department of Chemistry, Faculty of Science, University of Aleppo, Aleppo, Syria

*Corresponding author: Fax: +963 21 2633136; E-mail: dramadan@scs-net.org

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Gas chromatographic analysis of automobile gasoline and lighter gas using phenyl-modified Aleppo bentonite was developed. The particles of Aleppo bentonite which have diameter (150-250 µm) were thermally treated and washed by concentrated HCl. Aleppo bentonite was grafted by dimethyldichlorosilane, then, it was reacted with phenyl magnesium bromide ($B_A$phenyl). The surface properties of B_A and B_A phenyl were characterized by nitrogen adsorption at 77 K and differential thermal analysis. It was found that, the BET surface areas (S_{BET}) was 11.86 and 4.21 m^2/g, the total pore volume v_p was (0.0388 and 0.01547 mL/g) and the mean pores radii r_a were (65.43 and 73.49 Å), respectively. Thirty six hydrocarbons components in gasoline and seven in lighter gas were determined by using B_A phenyl as support in gas chromatographic analysis. The principle gasoline components groups (total C_5 to total C_{10}) were presented as follows: 0.001, 0.28, 14.76, 34.16, 13.07, 25.13, 11.59 and 0.76 % and lighter gas percent (propane, isobutane and *n*-butane) as follows: 3.03-48.49, 29.03-45.75 and 20.88-67.27 %, respectively.

Keywords: Phenyl-modified Aleppo bentonite, Gas chromatography, Gasoline, Lighter gas.

INTRODUCTION

Aleppo bentonite is rocky clay which consists of 47 % SiO_2, 14.4 % Al_2O_3 and some other oxides as Fe_2O_3, MgO, CaO, Na_2O, *etc.*[1,2]. The thermal treatment causes decreasing of its specific surface area with increasing in the temperature of thermal treatment[3,4]. Bentonite clays are used in many industrial processes[5,6] and it can be used as chromatographic supports in gas chromatography to separate many mixtures after grafting with different methods[7,8]. Bentonite is used as stationary phase in thin layer chromatography to separate some metal ions and vitamins B_1, B_6, B_{12}[9,10].

The surface properties of methyl- or octyl- or octadecyl-modified bentonite using nitrogen adsorption (BET) at 77 K, IR and differential thermal analysis (DTA) were studied. The surface areas (S_{BET}), the mean pores radii (r_a) and the total pore volumes were determined[9,10].

Based on detailed hydrocarbon analysis of gasolines, their fractional composition were measured[11-13]. Knowing the qualitative and quantitative composition of the gasolines, one can determine the content of *n*-paraffin, isoparaffin, aromatic hydrocarbons, naphthene and olefin (PIANO) groups of hydrocarbons as well as of oxyorganic compounds (alcohols and ethers) used to raise the octane number[14]. The opportunity for solving similar problems arises from application of high-resolution capillary columns that allow completed separation of all hydrocarbons components. Analytical systems with such columns makes stringent demands on standards of data processing systems, especially on the algorithm for automatic identification of the components.

Tabular data of the main hydrocarbons in gasolines was collected and systematized. A procedure has been worked out for detailed analysis of the hydrocarbon compositions and calculation of the key characteristics of unethylated automobile gasolines. The methods of calculation of the complex characteristics of these gasolines have been programmed and the developed software package has been integrated into the system Unichrom-97[15].

An automatic method has been developed for the determination of gasoline components by gas chromatography. Separation has been achieved on squalane and cross-linked OV-1 capillary columns[16]. Analytical conditions were optimized and all peaks were identified. Programmed temperature indices were used for automatic identifications. These indices appear to be reproducible on different capillary columns having the same commercial specifications with identical analytical conditions[17,18].

Study has been conducted on motor gasoline and natural gas with applying gas chromatography and physical/chemical analysis using ethyl alcohol (oxygenates). The physical, chemical and gas chromatograph analysis are compared. The physical analysis revealed the basic role of adulteration and gas chromatograph analyses provided by the adulteration[19-23].

This paper describes an automated method for the determination of gasoline and natural gas compounds by gas chromatographic analysis using packed column with support phenyl-modified Aleppo bentonite.

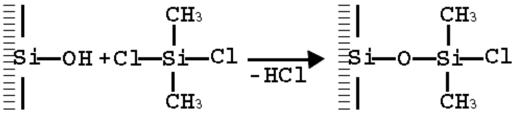
EXPERIMENTAL

The chromatograms were obtained by using a GC-9A gas chromatograph equipped with a flame ionization detector (FID) and chromatopac C-R3A printer (Shimadzu Co.), 1 µL syringe (Hamilton Co.). Surface area and pore size measurement (BET) were recorded using Micromeritics Gemini III 2375 under nitrogen atmosphere (USA). Differential thermal analysis (DTA), LINSEIS type STA PT-1600, Germany and pH meter from Radio meter company model Ion Check were used. Diluter pipette model DIP-1 (Shimadzu), having 100 µL sample syringe and five continuously adjustable pipettes covering a volume range from 20-5000 µL (model PIPTMAN P, GILSON), an ultrasonic processor model powersonic 405, electronic balance (Sartorius-2474; d = 0.01 mg), ash furnace at 100-1200 ºC type Nabertherm and oven at 50-350 ºC for treatment of bentonite were used.

Tetrahydroforan, dichloromethane, dimethyldichlorosilane, 1-bromophenyl, magnesium metal were purchased from Merck, Germany.

Preparation of thermal treatment and acidic washing for bentonite: Bentonite was crushed to obtain small pieces, which have diameter (150-250 µm) and was thermally treated in two steps at 700 ºC and then at 1000 ºC. After each step was refluxed with 6 N HCl at boiling point for 18 h to remove soluble oxides especially iron oxide. Then it was washed several times with distilled water and dried at 120 ºC for 3 h (B_A).

Bentonite chlorination (B_ACl): 30 g of washed bentonite (B_A) is dispersed in 250 mL of dichloromethane and 10 mL of dimethyldichlorosilane. The mixture was left under reflux during 3 h. The solvent was evaporated and the residue was dried at 280 ºC during 3 h. The chlorinated product was kept under inert nitrogen atmosphere (B_ACl), as the equation:

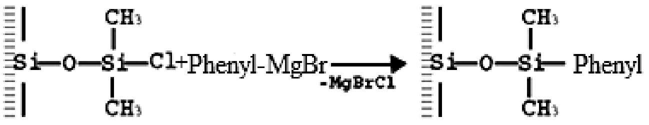


$$\equiv Si-OH + Cl-Si(CH_3)_2-Cl \xrightarrow[-HCl]{} \equiv Si-O-Si(CH_3)_2-Cl$$

Preparation of phenyl-modified Aleppo bentonite (B_A phenyl): Phenyl magnesium bromide was prepared from reaction 10.6 mL of 1- bromophenyl with 2.4 g of clean and dry magnesium in 200 mL of anhydrous tetrahydroforan (THF) as:

$$\text{Phenyl-Br} + \text{Mg} \xrightarrow[66\,°C]{THF} \text{Phenyl-MgBr}$$

The solution of phenyl magnesium bromide was added to chlorinated bentonite (B_ACl) under inert atmosphere (N_2). The mixture was allowed to reflux for 3 h. Then the heating was removed and contents were allowed to cool. The produce was filtered and washed with methanol and dried at 105 ºC for 2 h (B_A phenyl), as the equation:



$$\equiv Si-O-Si(CH_3)_2-Cl + \text{Phenyl-MgBr} \xrightarrow[-MgBrCl]{} \equiv Si-O-Si(CH_3)_2-\text{Phenyl}$$

RESULTS AND DISCUSSION

Surface properties of B_A and B_A phenyl: Specific surface areas of B_A and B_A phenyl were determined by the adsorption of nitrogen at 77 K (BET). For determination of textural properties, the adsorption was carried out until near saturation ($P/Po \approx 1.0$), then the desorption was completed until closure of the hysteresis loop. Representative adsorption-desorption isotherms of nitrogen for B_A and B_A phenyl are shown in Fig. 1. The isotherms are II and IV type of SING and BDDT classifications, which indicate the presence of mesoporous structure. Application of the linear BET equation to the nitrogen adsorption data was obtained within the range of relative pressures (0.02 – 0.25) was as the follows: $y = 0.36726x + 0.0012$ and $y = 1.035x + 0.0029$ for B_A and B_A phenyl, respectively. BET specific surface areas (S_{BET}) were 11.86 and 4.21 m^2/g , the total pore volume v_p (0.0388 and 0.01547mL/g) was determined from the adsorbed volume at $P/Po = 0.95$ in the liquid form and the mean pores radii r_a (65.43 and 73.49 Å), was determined from the equation: $r_a = 2 \times 10^4 \times v_p/S_{BET}$, for B_A and B_A phenyl, respectively. The variation of specific surface area, total pore volume and mean pores radii causing by grafting modification, as seen in Table-1.

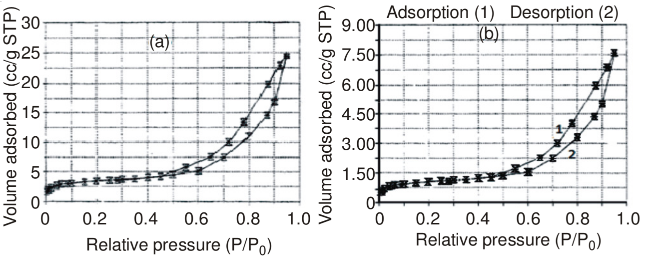


Fig. 1. Adsorption-desorption isotherm of nitrogen at 77 K on B_A (a) and on B_A phenyl (b)

TABLE-1
SURFACE PROPERTIES OF B_A AND B_A PHENYL

Support	S_{BET} (m^2/g)	v_p (mL/g)	r_a (Å)
B_A	11.86	0.0388	65.43
B_A Phenyl	4.21	0.01547	73.49

It was noticed that the specific surface area and the total pore volume were decreased from (11.86 m^2/g and 0.0388 mL/g) to (4.21 m^2/g and 0.01547 mL/g), respectively and the mean pores radii increased from 65.43 to 73.49 Å (Table-1 and Fig. 2).

Differential thermal analysis (DTA): A useful method for the characterization of B_A and B_A phenyl was measured by differential thermal analysis (DTA) technique in air atmosphere using 40 mg bentonite with α-Al_2O_3 as reference and heating rate 10 ºC/min. Fig. 3 shows that, the DTA traces of the B_A and B_A phenyl. It exhibited two endothermic peaks. The first appears at 145 ºC, which is corresponding to the loss of water of hydration. The second, which occurred at about 610 ºC,

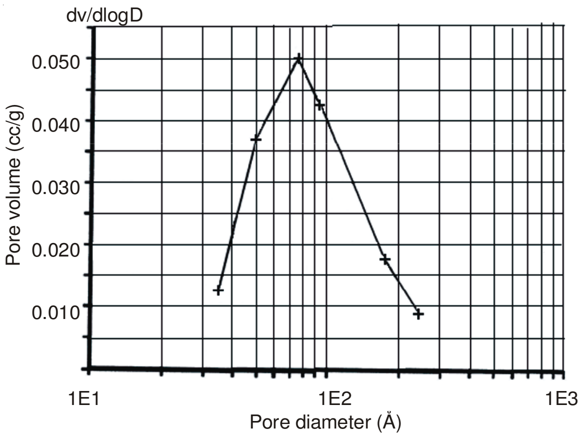


Fig. 2. Pore volume distribution of B_A phenyl sample

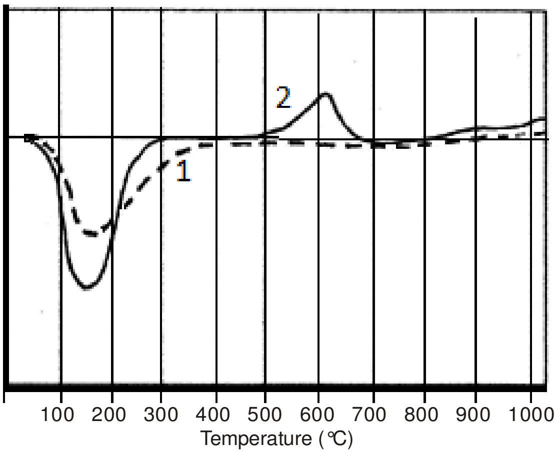


Fig. 3. Differential thermal analysis curve for B_A (1) and B_A phenyl-modified (2). (in air atmosphere using 40 mg bentonite with α-Al_2O_3 as reference and heating rate 10 °C/min)

is related to the burning of hydrocarbon (phenyl) in B_A phenyl support.

Hydrophobicity: Hydrophobicity estimation before and after modification, by comparing the dispersiblility of the B_A and B_A phenyl in water and benzene. Fig. 4 showed that the B_A dispersing was in water layer only. By opposition, the presence of hydrophobic alkyl group on the external surface of B_A phenyl, made the B_A phenyl deposited in organic phase at the benzene-water.

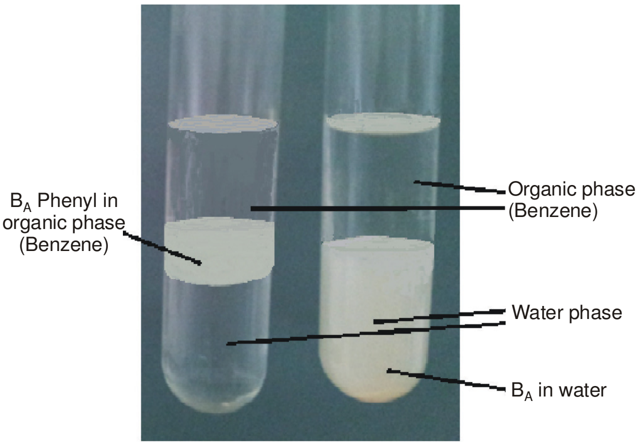


Fig. 4. B_A (right) and B_A phenyl (left) dispersed in water/benzene (organic phase) system

Plotting the relation between variation of the logarithm of retention volume and the reverse of absolute temperature log Vs = f(1/T): The modification superficial structure of grafted B_A phenyl compared to B_A was studied by "inverse gas chromatographic method" in the range 40-110 °C and column dimension (100 cm × 4 mm) using dichloromethane (polar), benzene (moderate polarity) and *n*-pentane (non-polar) as auxiliary solutes. The plotted relationship log Vs = f(1/T) shown that, a decreasing of volume retention was noticed with grafted bentonite by modification phenyl group compared to B_A (Fig. 5). Fig. 5 shown that the three auxiliary solutes approve the modification of the superficial structure of the bentonite B_A support surface.

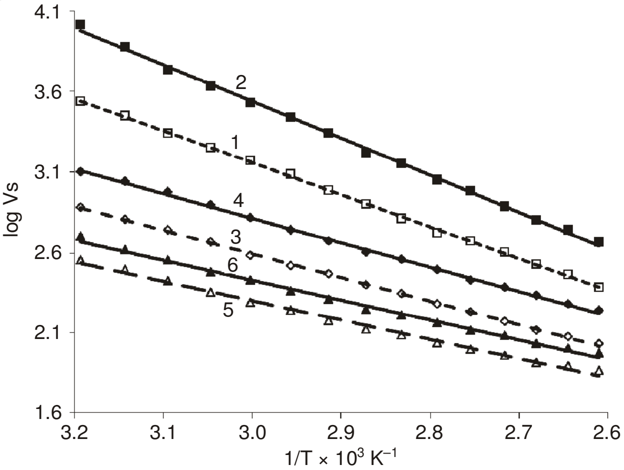
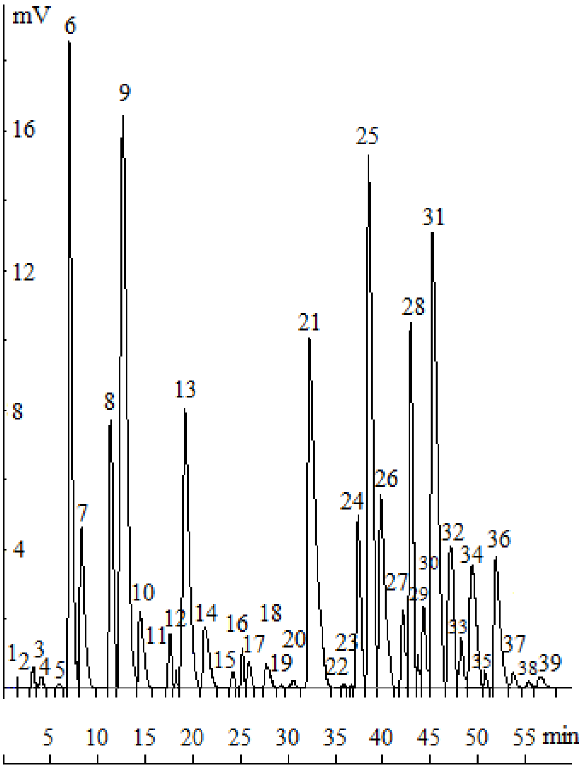


Fig. 5. Variation of log Vs = f(1/T) on (100 cm × 4 mm) packed columns using bare bentonite B_A (2, 4, 6) and grafted bentonite B_A phenyl (1, 3, 5); benzene (1, 2); dichloromethane (3, 4); *n*-pentane (5, 6)

Identification of gasoline: An automatic method has been developed for the determination of gasoline components by gas chromatography using grafted Aleppo bentonite (B_A phenyl). The chromatographic conditions for analysis are as the following: analytical copper column (100 cm × 4 mm) packed with B_A phenyl, programmed column temperature between 35-215 °C, with increasing temperature rate 3 °C/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 0.2 μL and injected port temperature 190 °C. Fig. 6 shows the gasoline chromatogram. The analytical results were characterized by high precision, accuracy and reproducibility. The components groups of gasoline was given in Table-2.

TABLE-2
CARBON NUMBER OF COMPONENTS GROUPS IN GASOLINE

Carbon number (Identity)	Amount (%)
Total C_3	0.0008948
Total C_4	0.28
Total C_5	14.76
Total C_6	34.16
Total C_7	13.07
Total C_8	25.13
Total C_9	11.59
Total C_{10}	0.76
Total	99.75
Total C_5-C_{10}	99.47



Rank	Time, min	Area%	Area	Name
1	0.026	0.001245	69	?
2	1.458	0.0008948	50	Propane
3	3.103	0.1564	8700	Isobutane
4	3.770	0.1225	6815	n-Butane
5	5.825	0.02161	1202	?
6	6.992	8.44	469464	Isopentane
7	8.216	2.747	152831	n-Pentane
8	11.323	3.574	198816	2-Methyl butane
9	12.599	14.02	792366	2,3-Dimethyl butane
10	14.408	1.422	79100	2-Methyl pentane
11	17.633	0.6623	36843	3-Methyl pentane
12	18.253	0.1651	9186	Isohexane
13	19.121	6.896	383587	n-Hexane
14	21.245	1.471	81812	2,4-Dimethyl pentane
15	24.313	0.2181	12132	2-Methyl hexane
16	25.216	0.4567	25404	Methyl Cyclopentane
17	25.731	0.43	23920	3-Methyl hexane
18	27.775	0.5114	28447	Isoheptane
19	29.262	0.05789	3220	n-Heptane
20	30.545	0.1724	9589	n-Octane
21	32.229	10.54	586316	Benzene
22	35.222	0.0218	1212	2,2-Dimethyl pentane
23	35.961	0.0207	1152	2-Dimethyl heptane
24	37.343	2.875	159924	2,3,4-Trimethyl pentane
25	38.435	10.34	575414	Toluene
26	39.703	4.502	250444	2,3-Dimethyl hexane
27	42.036	1.036	57653	2-Methyl octane
28	42.878	5.155	286731	Ethyl benzene
29	43.653	0.2706	15054	m-Xylene
30	44.194	1.195	66498	p-Xylene
31	45.134	10.96	609874	o-Xylene
32	47.138	3.279	182394	1-Methyl-3-ethyl benzene
33	48.117	0.711	39549	1,3,6-Trimethyl benzene
34	49.283	3.496	194471	1,2,4-Trimethyl benzene
35	50.210	0.200	12200	?
36	51.797	3.065	170493	1,2,3-Trimethyl benzene
37	53.655	0.2782	15477	1,4-Dimethyl-2-ethyl benzene
38	55.313	0.1212	6744	1,4-Diethyl benzene
39	56.539	0.3616	20116	Diethyl benzene
Total		100	5575269	

Fig. 6. Gas chromatographic analysis of gasoline components (Programmed column temperature between 35-215 ºC, with increasing temperature rate 3 ºC/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 0.2 µL and injected port temperature 190 ºC)

Identification of lighter gas (as gas refill lighter): The lighter gas components of three gas refill lighter were determined by gas chromatography using grafted Aleppo bentonite (B_A phenyl). The following commercial types were subjected to the analytical procedures: Won Bao, Butane Gas Products Refill (155 mL), China. Can, Gaslighter (250 mL), Egypt. Campingman, Butane Gas (227 g), Korea.

The chromatographic conditions for analysis are as the following: analytical copper column (100 cm × 4 mm) packed with B_A phenyl, programmed column temperature between 35-215 ºC, with increasing temperature rate 3 ºC/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 250 µL and injected port temperature 190 ºC. Fig. 7 shows that, the separation was completed with a high precision and reproducibility. The analytical results were characterized by high precision, accuracy and reproducibility. The carbon number of natural gas in studied gas refill lighter was observed in Table-3.

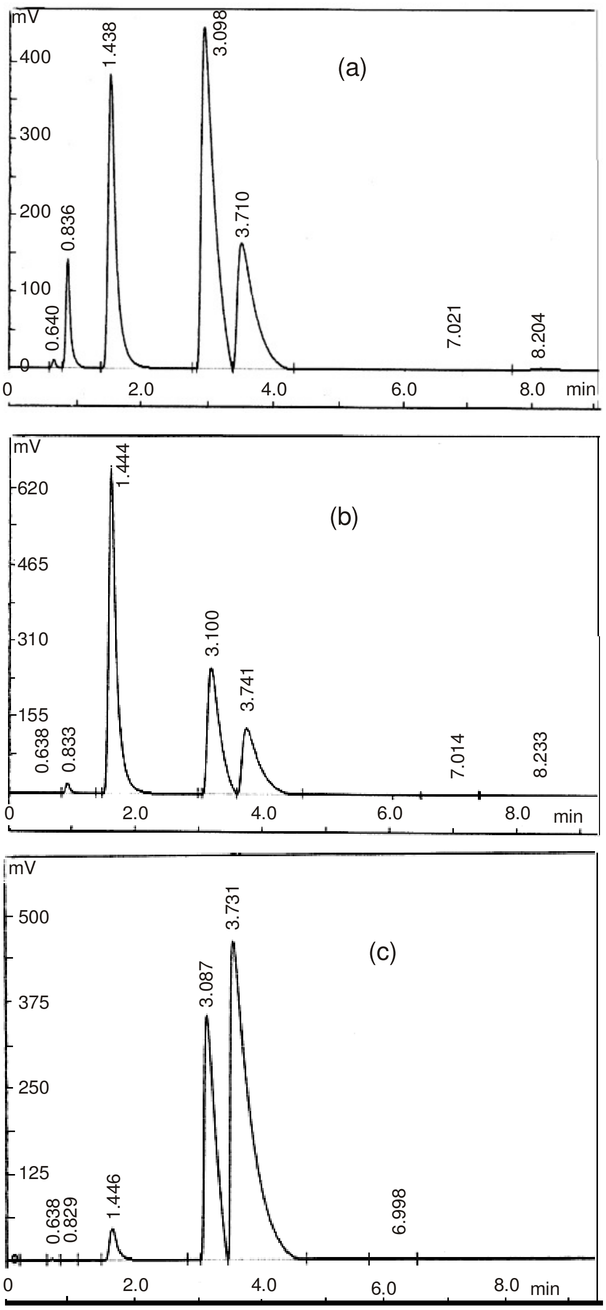


Fig. 7. Gas chromatographic analysis of natural gas components of three gas refill lighter: (a) Won Bao, Butane Gas Products Refill, China; (b) Can, Gaslighter, Egypt; (c) Campingman, Butane Gas, Korea (Programmed column temperature between 35-215 ºC, with increasing temperature rate 3 ºC/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 250 µL and injected port temperature 190 ºC)

TABLE-3
CARBON NUMBER OF LIGHTER GAS
IN STUDIED GAS REFILL LIGHTER

Carbon number (Identity)	Wan Bao, China (%)	Can, Egypt (%)	Camping man, Korea (%)
C_1 (Methane)	0.3305	0.002686	0.002658
C_2 (Ethane)	5.367	0.9382	0.06606
C_3 (Propane)	25.01	48.49	3.027
C_4 (Isobutene)	45.75	29.03	29.44
(*n*-Butane)	22.76	20.88	67.27
C_5 (Isopentane)	0.09771	0.08997	0.1474
(*n*-Pentane)	0.6776	0.5696	–
Total	99.993	100.00	99.953

Conclusion

Phenyl-modified Aleppo bentonite (B_A phenyl) as support for GC was developed. The BET surface areas (S_{BET}) for B_A phenyl was 4.21 m^2/g , the total pore volume (v_p) was 0.01547 mL/g and the mean pores radii (r_a) were 73.49 Å. Thirty six hydrocarbons components in gasoline and seven in lighter gas were determined by using B_A phenyl as support in GCA. The principle gasoline components groups (total C_5 to total C_{10}) percent were presented as follows: 0.001, 0.28, 14.76, 34.16, 13.07, 25.13, 11.59 and 0.76 % and lighter gas per cent (propane, isobutane and *n*-butane) as follows: 3.03-48.49, 29.03-45.75 and 20.88-67.27 %, respectively.

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