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MINIMIZING EVAPORATION OF LIGHT HYDROCARBONS FOR IRAQI GASOLINE USING FATTY ACID ESTERS COMPOUNDS, SYNTHESIS AND CHARACTERIZATION

Mohammed Adnan Mansor and Abdullah Hussein Kshash*

Department of Chemistry, College of Education for Pure Science, University of Al-Anbar, Ramadi, Iraq.
*e-mail: drabdullahkshash@gmail.com

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ABSTRACT : The work includes synthesis of new fatty acids esters and thioesterby the reaction of 5-hydroxy isophthalic acid, glycolic acid and thioglycolic acid with fatty acidschloride,all reactions were monitored by TLC. Synthesized compounds were characterized by FT-IR, ^{1}HNMR, ^{13}CNMR and mass spectroscopy. The possibility of reducing evaporation light hydrocarbons from Iraqi gasoline was performed by introducing micro-quantities of synthesized esters as a new method. The efficiency of this method was evaluated by measuring saturated vapor pressure (Reid Vapor Pressure) at 37.8^{0}C, while surface tension at 25 ^{0}C of the concentrations (1-10 mg L^{-1}). The results indicate a successful attempt to use esters and thioesters compounds as reduce pressure agents. Optimal concentration was estimated by the lowest saturated vapor pressure.

Key words : Fatty acid ester, glycolic acid, gasoline pressure, Reid vapor pressure, thioglycolic acid.

INTRODUCTION

Gasoline is one of the petroleum materials, it can be divided into two types, from normal to excellent, while another classification takes into account the octane number to three types (Sheet *et al*, 2008). Such forms are obtained by petroleum distillation ranging from 38 to 150-205°C, some compounds are usually added as Antiknock simple to start (Butkus and Pukalskas, 2004), antioxidants (Gasoline Refining Testing) etc. Since gasoline contains light hydrocarbons, gasoline has become a volatile liquid that causes vapor pressure, which is one of the important properties of gasoline mixtures (Kshash *et al*, 2018). In this method, the liquid vessel and vapor chamber are connected and then heated in a bath to 37.8°C. Through evaporating from the refining, storage, and refueling phase, light hydrocarbons are lost, this evaporation leads to an increase in the concentration of these compounds in the air as well as creating environmental and economic problems (Farhan and Magaril, 2011; Abuzova, 1975; Shamae, 1980) due to environmental and economic problems for evaporation, this problem requires fast treatments and effective solutions to minimize or restrict it, especially in countries with temperatures above 45°C in the summer season. There have been various attempts to reduce the evaporation of light hydrocarbons from gasoline using different chemical structures as additives. These attempts were to use micro-concentrations of fatty acids (Farhan *et al*, 2017) 1,6-Di-O-(4-Alkanoyloxybenzoyl)-D-glucitol (Kshash and Ismail, 2018). This paper aims to synthesize simple ester compounds that are used to minimize the pressure of Iraqi gasoline by the formation of micelles due to these compounds possess non-polar and polar segments.

MATAERIALS AND METHODS

Materials and instruments

Glycolic acid, 5-hydroxy isophthalic acid, thioglycolic acid, Lauric acid, Myristic acid, Palmitic acid, Stearic acid, and thionyl chloride were supplied by Sigma-Aldrich Chemical Co. used without further purification, solvents Scharlau Chemical Company, melting points were measured on JANEWAY device. Bruker-Tensor 27 Spectrometer used to record Infrared spectra, Bruker-500 MHz spectrometer used to recorded NMR spectra using DMSO-d_6 as a solvent, Mass spectroscopy recorded by Agilent Technology Model: 5973.

Synthesis of fatty acid chloride compounds

In 100 mL round-bottomed flask, 30 gm fatty acid was added to 40 mL thionyl chloride, the mixture refluxed at 75°C in a water bath for 2 hours. Thereafter, excess of thionyl chloride was distilled to give the desired liquid

fatty acid chlorides.

Synthesis of ester and thioester compounds

To 50 mL round-bottomed flask containing 20 mL pyridine and (3 mmol) hydroxyl or thiol compound immersed in ice was added (3 mmol) of fatty acids chlorides under N_2 gas flow, the mixture was stirred overnight at RT. Thereafter, the mixture was acidified with 10 mL of 25 percent HCl and then poured with stirring on crush ice, the solid product was filtered, washed with water successively, recrystallized from ethanol.

RESULTS AND DISCUSSION

Synthesis

The desired ester and thioester were synthesized according to the route illustrated in Scheme 1.

The scheme was shown exothermic esterification reactions of hydroxyl and thiol group; therefore, the reactions were carried out in the ice.

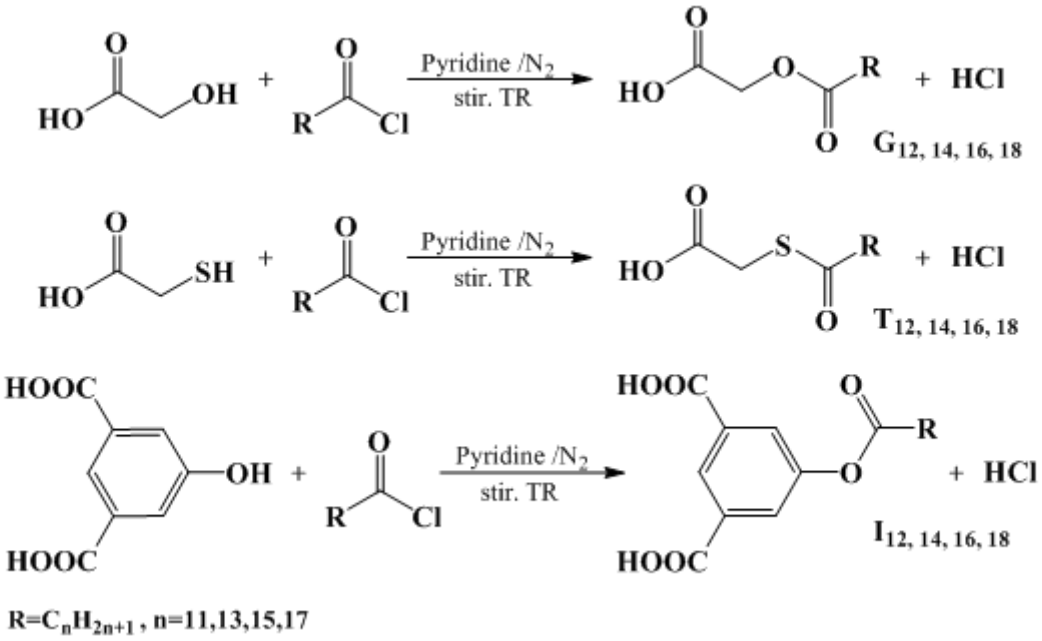
Characterization

Fatty acids chlorides : The synthesized fatty acids chlorides were characterized by FT IR were spectra showed disappearance of stretching vibrations of íO-H for hydroxyl group and the appearance of stretching vibrations of íC=O with higher wavenumber, besides some other absorption bands, data are listed in Table 1.

Characterization for synthesized esters and thioesters compound : The synthesized compounds were characterized by FT IR, the spectra were indicated

Table 1 : Selected FTIR absorption bands for fatty acids chlorides.

n=11,13,15,17		$C_nH_{2n+1}COCl$	
n	íC-$H_{Aliph.}$	íC=O	γ CH_2
12	2924	1796	720
14	2922	1797	720
16	2921	1797	721
18	2922	1797	720



Scheme 1 : Synthetic route of surfactant compounds.

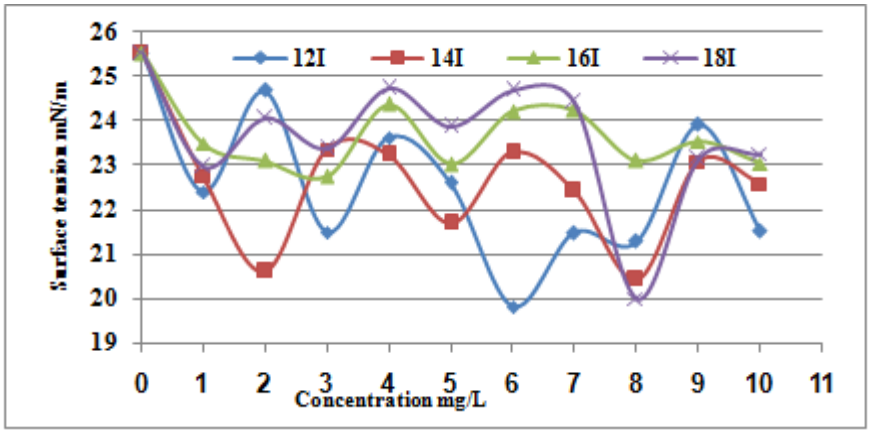


Fig. 1 : Surface tension for I compounds.

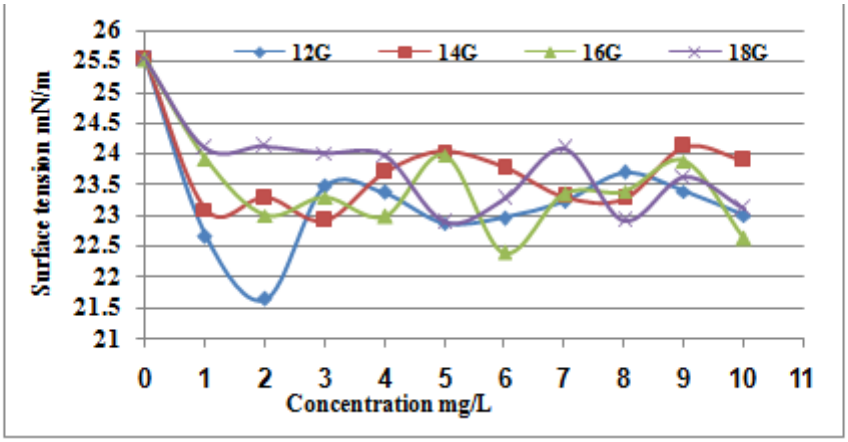


Fig. 2 : Surface tension for G compounds.

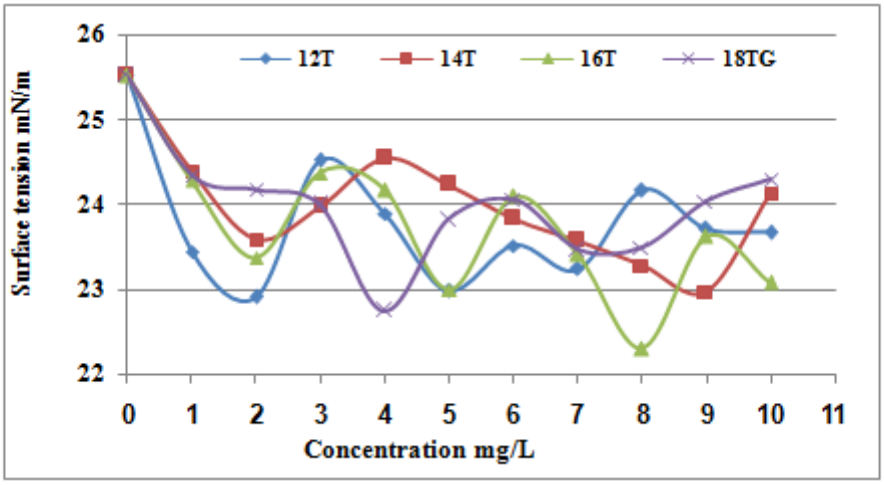


Fig. 3 : Surface tension for T compounds.

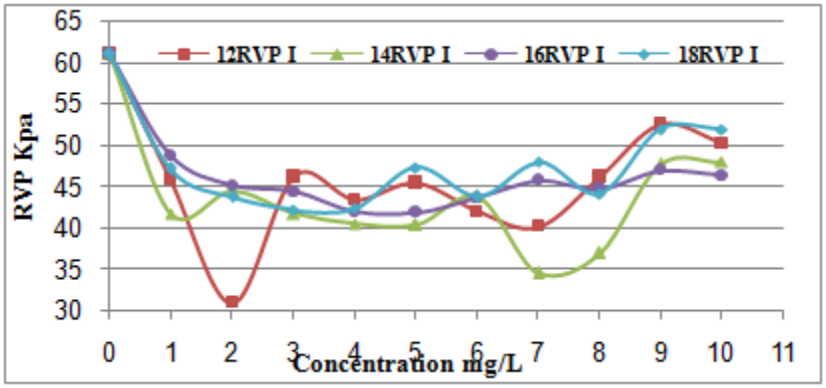


Fig. 4 : Saturated vapor pressure for I compounds.

the appearance of stretching vibrations of íC=O for ester and thioester, besides some other absorption bands, data are listed in Table 2.

While, ^{1}H-NMR spectra for all compounds showed triplet signal within the range 0.84-0.86 ppm attributable for methyl group C$\underline{H}_3$, multi-signal was observed within the range 1.13-1.74 ppm attributable to (C$\underline{H}_2$)$_n$, triplet signal 2.19-2.61 ppm attributable for áC$\underline{H}_2$, for Isophthalic ester aromatic protons were observed as multi-signal at range 7.23-8.35 ppm, while the signal for methylene group (C$\underline{H}_2$-O, C$\underline{H}_2$-S) was identified as singlet signal at a range 4.03-4.54 ppm, also a proton signal of the carboxyl group was observed as a singlet signal within the range 12.78-13.44 ppm, data are listed in Table 3.

To validate the chemical structures, synthesized compounds were characterized by 13C NMR spectrum, data are given in Table 4.

Table 2 : FTIR absorption bands for ester and thioester compounds.

Symb.	νC-H		νC=O		νC=C arom	γCH$_2$
	Arom.	Aliph	Ester, thioester	Carboxy.		
I_{12}	3006	2918	1757	1711	1596	723
I_{14}	3020	2917	1757	1713	1596	723
I_{16}	3051	2917	1757	1714	1596	717
I_{18}	3046	2916	1757	1714	1596	718
G_{12}	-	2916	1755	1722	-	718
G_{14}	-	2916	1755	1723	-	718
G_{16}	-	2916	1755	1722	-	718
G_{18}	-	2915	1756	1722	-	717
T_{12}	-	2916	1682	1682	-	718
T_{14}	-	2913	1682	1682	-	717
T_{16}	-	2913	1682	1682	-	717
T_{18}	-	2914	1682	1682	-	717

Table 3 : ^{1}H NMR for ester and thioester compounds.

Symb.	C**H**$_3$	(C**H**$_2$)$_n$	áC**H**$_2$	C**H** Arom.	C**H**$_2$-O C**H**$_2$-S	COO**H**
I_{12}	0.84 t	1.23-1.68 m	2.61 t	7.87-8.35 m	-	13.44 s
I_{14}	0.85 t	1.13-1.65 m	2.60 t	7.23-7.55 m	-	13.34 s
G_{12}	0.85 t	1.24-1.55 m	2.34 t	-	4.53 s	12.78 s
G_{14}	0.86 t	1.25-1.57 m	2.35 t	-	4.54 s	12.99 s
G_{16}	0.85 t	1.24-1.55 m	2.34 t	-	4.53 s	12.96 s
G_{18}	0.84 t	1.23-1.54 m	2.33 t	-	4.53 s	13.01 s
T_{12}	0.85 t	1.24-1.59 m	2.19 t	-	4.03 s	13.01
T_{14}	0.86 t	1.24-1.74 m	2.20 t	-	4.04 s	13.18
T_{16}	0.85 t	1.24-1.57 m	2.20 t	-	4.04 s	13.00
T_{18}	0.86 t	1.24-159 m	2.20 t	-	4.04 s	13.06

Table 4 : ^{13}C NMR for ester and thioester compounds.

Sy.	C**H**$_3$	(C**H**$_2$)$_n$	áC**H**$_2$	C**H** Arom.	C**H**$_2$-O C**H**$_2$-S	C=O	
						Carbox.	Ester
I_{12}	13.73	21.90-31.11	33.22	126.52-150.46	-	165.60	171.49
I_{14}	13.37	21.53-30.73	32.84	126.15-150.08	-	165.22	171.13
G_{12}	13.36	21.54-28.45	32.56	-	59.84	168.54	171.89
G_{14}	13.89	22.07-29.03	33.10	-	60.37	169.07	172.42
G_{16}	13.87	22.09-29.07	33.65	-	60.35	169.04	172.38
G_{18}	14.01	22.24-29.21	33.81	-	60.53	169.20	172.51
T_{12}	14.07	22.25-33.82	33.82	-	43.07	169.74	197.79
T_{14}	13.37	21.55-30.75	33.12	-	42.36	169.04	197.10
T_{16}	13.37	21.55-30.76	33.12	-	42.36	169.04	197.08
T_{18}	13.36	21.54-30.74	33.12	-	42.37	169.03	197.08

Surfactant properties

Surface tension measurements : Surface tension measurements consider as an important indication for studying aggregation behavior of nonionic surface-active agents compounds. Surface tension for synthesized compounds was evaluated for concentrations (1 - 10 mg L-1) at 25ºC, using capillary tube method, results are listed in Table 5.

Results revealed that all synthesized compounds possess surface-active properties due to their decreasing surface tension of Iraq gasoline. Moreover, the Surface tension was associated with surfactant concentration

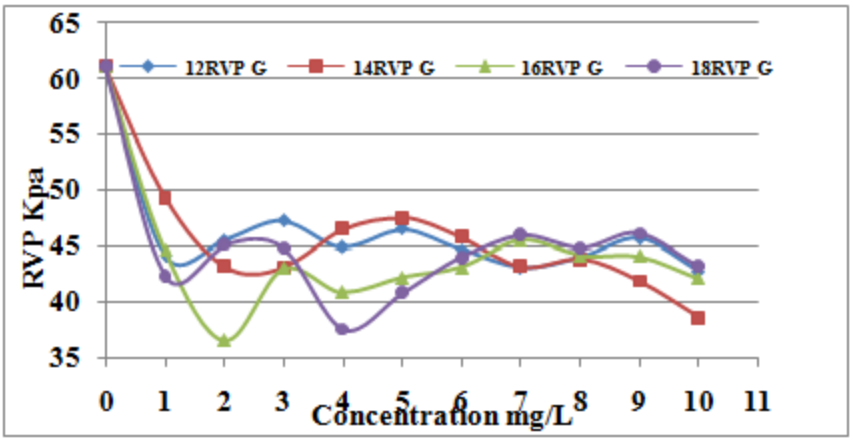


Fig. 5 : Saturated vapor pressure for G compounds.

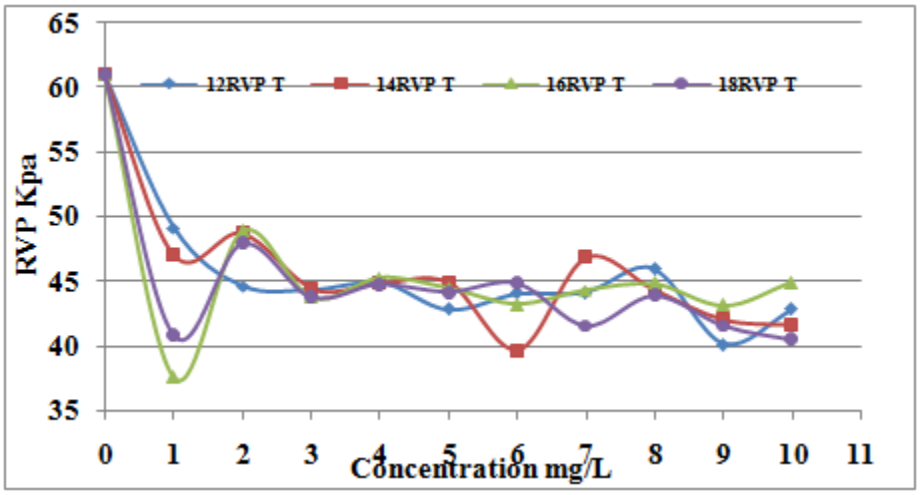


Fig. 6 : Saturated vapor pressure for T compounds.

Table 5 : Surface tension mN/m for synthesized compounds.

Conc. (Mg/L)	Surface Tension mN/m											
	T_{12}	T_{14}	T_{16}	T_{18}	T_{12}	T_{14}	T_{16}	T_{18}	T_{12}	T_{14}	T_{16}	T_{18}
0	25.51	25.51	25.51	25.51	25.51	25.51	25.51	25.51	25.51	25.51	25.51	25.51
1	22.40	22.76	23.49	22.98	22.66	23.09	23.91	24.08	23.45	24.39	24.29	24.34
2	24.67	20.62	23.09	24.06	21.64	23.28	23.00	24.12	22.91	23.58	23.37	24.18
3	21.49	23.35	22.73	23.38	23.46	22.91	23.29	24.00	24.52	23.98	24.37	24.00
4	23.62	23.24	24.36	24.73	23.37	23.70	22.98	23.97	23.90	24.54	24.17	22.75
5	22.60	21.70	23.02	23.86	22.86	24.03	23.97	22.89	22.98	24.23	22.99	23.82
6	19.82	23.29	24.20	24.69	22.95	23.77	22.39	23.26	23.52	23.83	24.10	24.06
7	21.48	22.43	24.22	24.42	23.22	23.30	23.34	24.08	23.24	23.57	23.40	23.46
8	21.28	20.43	23.10	20.00	23.69	23.27	23.39	22.90	24.17	23.28	22.30	23.49
9	23.90	23.08	23.52	23.15	23.39	24.11	23.87	23.61	23.71	22.97	23.62	24.04
10	21.52	22.58	23.03	23.26	23.00	23.89	22.62	23.11	23.68	24.13	23.08	24.30

(Figs. 1, 2 and 3).

Saturated vapor pressure : Saturated vapor pressure (Reid Vapor Pressure RVP) was evaluated, by preparation of concentrations (1 - 10 mg L^{-1}) for all synthesized compound, the results were various due to the hydrocarbon chain length for fatty acid, data are listed in Table 6 and Figs. 4, 5 and 6.

CONCLUSION

Ester and thioester compounds have been successfully synthesized and characterized by FTIR, 1H NMR and 13C NMR. Their potential as a surface-active agent was demonstrated by reducing surface tension and saturated vapor pressure of Iraqi gasoline, contributing to their use in minimizing evaporation of gasoline thereby

Table 6 : Saturated Vapor Pressure (kPa) for synthesized compounds.

Conc. (Mg/L)	Reid vapor pressure (RVP)											
	T_{12}	T_{14}	T_{16}	T_{18}	T_{12}	T_{14}	T_{16}	T_{18}	T_{12}	T_{14}	T_{16}	T_{18}
0	61.0	61.0	61.0	61.0	61.0	61.0	61.0	61.0	61	61	61	61
1	46.0	41.8	48.8	47.2	44.1	49.3	44.5	42.3	49.1	47	37.5	40.8
2	31.0	44.5	45.2	43.8	45.5	43.1	36.5	45.1	44.6	48.7	48.8	47.9
3	46.2	41.8	44.4	42.2	47.2	43.0	42.9	44.8	44.3	44.4	43.7	43.7
4	43.4	40.5	42.0	42.4	44.9	46.5	40.8	37.5	44.9	44.8	45.2	44.7
5	45.5	40.4	41.9	47.3	46.5	47.5	42.1	40.8	42.8	44.9	44.4	44.1
6	42.0	43.8	43.7	43.8	44.6	45.8	43.0	43.9	44	39.6	43.2	44.8
7	40.2	34.6	45.8	48.0	43.0	43.1	45.5	46	44.1	46.8	44.3	41.5
8	46.2	37.0	44.8	44.2	44.0	43.7	44.1	44.8	45.9	44.3	44.8	43.9
9	52.5	47.7	47.0	52.0	45.7	41.8	44.0	46.1	40.1	42	43.1	41.5
10	50.2	48.0	46.4	51.9	42.7	38.5	42.0	43.1	42.8	41.6	44.9	40.5

reducing environmental pollution as well as reducing economic losses.

REFERENCES

Abuzova F F (1975) *Thesis for the Degree of Doctor of Technical Sciences*. Ufa 1975: 334.

Butkus A and Pukalskas S (2004) The Research into the Influence of Ecological Petrol Additives in the Automobile Laboratory..

Farhan Ed. M M and R Z Magaril (2011) Oil and Gas of Western Siberia: Materials of theInternational Scientific-technical. Dedicated to the 55th Anniversary of Tyumen State Oil and Gas University. Tyumen: Tyumen State Oil and Gas University 217-220.

Farhan M M, Al-jumialy M M, Al-muhammadi A D and Ismail A S (2017) *Energy Procedia* **141**, 471- 478.

Gasoline Refining and Testing page 2, 3, and 4.

Kshash A H and Ismail A S (2018) Minimizing evaporation of light hydrocarbons for Iraqi gasoline by using D-glucitol fatty acid esters as reduced pressure agents, synthesis and characterization. *Petroleum and Coal* **61**(1), 100 – 109.

Shamae S K (1980) *The place of the oil industry in Iraq*, Baghdad (Iraq): Dar al-Rashid. 1980: 285.

Sheet E A and Hamadi A S (2008) *M.Sc. thesis*, Republic of Iraq, Ministry of Higher Education & Scientific Research, University of Technology.