FORMATION OF NANOSTRUCTURED MATERIALS USING WASTE ENGINE OIL

Mahmudov H.M.,Ismayilova M.K.,Hasanov S.H
Laboratory of energy consuming radiation processes, Institute of Radiation Problems,
Azerbaijan National Academy of Sciences
AZ1143 Baku, Azerbaijan 9, Bakhtiyar Vahabzadeh str.

ismayilovamehpara@gmail.com

hokman.mahmudov@gmail.com

Abstract. The present work deal with the development of new chemical method to prepare green fuel by using waste oil products , such as waste engine oil.Nanostructured composite was prepared via treatment waste engine oil (WEO) by metal oxide nanoparticles, with diameter 20-50 nm. Effect of concentration of Al_2O_3 nanoparticles on WEO has been studied by FT-IR spectroscopy method .The thermal behaviour of nano- complexes formed with metal oxide nanoparticles was studied by derivatograph.The thermal decomposition of the complexes was also investigated. It is shown that with 0,0001-0,0 wt. % Al_2O_3 contents in composite are observed most effective changes in rheological and thermal physical parameters.The received results are explained with the supramolecular structure of the materials.

Key words:waste engine oil, nanoparticles, rheological parameters, thermal parameters

1.INTRODUCTION.

Converting used engine oil to useable product is very actual.Waste Engine Oils (WEO **)** presents a complete description of the field of engine used oils, widely collected in the networks of services-stations and garages[1].Composite of carbon materials with other metal oxides or nanostructured materials can be studied in order to meet the other desired applications. Intensive studies on the other properties of carbon materials from WEO such as mechanical, optical, thermal and magnetic properties are needed to be performed in order to expand their applications. Due to hydrophobic, hydrophilic and pseudo plastic nature as well as saving in materials it's expected economic benefits from the application of these nanostructured materials in different branches of oil industry (drilling, enhanced oil recovery and etc.) [2].The rheological properties of waste industrial oil has been studied and investigated that after treatment waste material by Al nanoparticles the rheological parameters of obtained composite are improved [2-3]. It has been explained the correlation with structure and properties of composition. It was studied nanosystems' structural characteristics by means of IR spectroscopy method and investigated the effects of Al_2O_3nanoparticles on the rheological parameters [4].In many currently explored applications of organic-inorganic hybrid materials, the achievement of superior properties is often hampered by the weak chemical (i.e. van der Waals, hydrogen bonding) interactions existing between the inorganic building blocks, leading, *inter alia*, to leaching of the inorganic components, agglomeration, phase separation, low mechanical stability. This is particularly critical for heterogeneous catalysis applications.

Recent years there has been a great deal of research on the subject of nanostructured materials. Many nanostructured materials have been and are being prepared with increasing control over molecular configurations, conformations, and supramolecular assembly. These nanomaterials place an increasing challenge for characterization techniques to confirm the proposed structure and morphology [5]. From these methods Fourier Infrared (FT-IR) Spectroscopy is very interesting and gives important informations about structure change.Taking the above into consideration, by methods of FT-IRSpectroscopy was studied the features of structural changes, which observed in the nanoheterogeneous systems based on waste engine oil (WEO) and Al_2O_3 nanoparticles, depending on changes of concentration of nanoparticles.

2.EXPERIMENTAL PART

IR spectra were taken with FT-IR Spectrometer Varian 640-IR in frequency range 4000–400cm^{-1} at room temperature. The absorption spectra of the samples were obtained as form of a thin layer on the KBr boards.Two KBr prisms were used to constitute the interferometer cavity. TGA was studied atPerkin Elmer STA 6000 (t ~ 20-990˚C, heating in N_2 medium).Thermal behaviour of these complexes have been investigated by TG and DTA techniques in static air atmosphere.Termoqrams of initial and nanocomposites have been determined in the temperature range of 303- 773K on STA 600 Derivatoqraf(Perkin Elmer).

By varying the amount of Al_2O_3 (d=20-50nm) nanoparticles impacting on WEO, obtained the nanocomposites with new structural-mechanical and thermal properties.The Al_2O_3 nanoparticles in different concentrations: 0, 0001; 0,001; 0,005; 0,01; 0,05; 0,1; 0,5; 1,0%; were added to the WEO and after this there has been investigatedthe changes in their chemical content and structure.

3.DISCUSSION OF THE RESULTS

The IR absorption spectra of these samplesare given in the figure 1. Spestrum 1 presents the infrared spectra of the ordinary waste engine oil, i.e. initial compound(waste engine oil). In this spectrum, it is possible to identify following frequencies of absorption bands with several maximums:

• 3070 cm^{-1} - stretch vibrations of -C = C alkans

•2950 cm^{-1}-asymmetric stretch vibrations of methyl (CH_3) groups

•2923 and 2853 cm^{-1} –symmetric and asymmetric stretch vibrations of CH_2 groups

• 1457 and 1376 cm^{-1}-asymmetric (as) and symmetric (s) deformation vibrations of methyl (CH_3) groups

• 720 and 660 cm^{-1}- pendulum vibrations of $(CH_2)_n$

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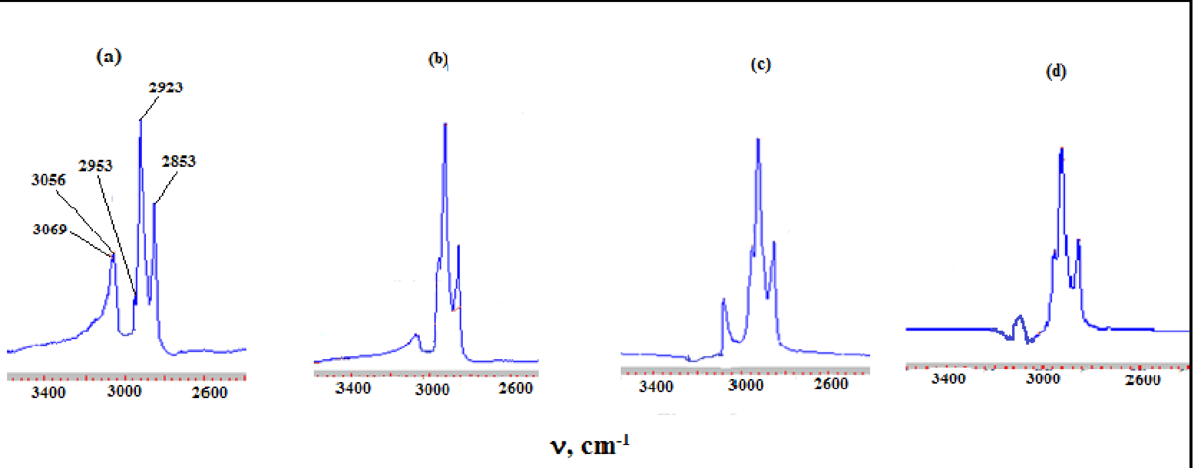

Fiq. 1

Fig.1.FT-IR spectra of initial (a) and nanostructured WEO:WEO +0,001mass% Al_2O_3 (b) ; WEO +0,01 mass% Al_2O_3 (c); WEO + 0,1% mass Al_2O_3 (d)

As seen from Figure 1, in the IR spectra 2 of nanocompositeobtained by mixing of waste engine oilwith Al_2O_3 nanoparticles (where consentration of nano Al_2O_3 content is 0,001 mass.%)several changes can be observed. Comparative analysis of the infrared absorption spectra between WEO and nanostructured WEO(spectrum 1 and specrtum 2) allows to say the following:

1. Thereis no change in the frequency value of maximums inthe range 4000-400 cm^{-1}which corresponds to the absorption frequencies of methyl (CH_3) and methylene (CH_2) groups,that is the functional structure of substances (waste engine oil and nanocomposites).New absorption bands maximumsare not observed.
2. The absorption coefficient (J) of nanocomposite (nanostructured WEO) inrange 4000 – 400 $cm^{-1}$is increased several times (J/J_0 = 2-3) compared to the absorption coefficient of the initial substance-waste engine oil(J_0).In its turn this change is accompanied by the changingof intensities (J) of the absorption bands of methyl(CH_3) and methylene (CH_2) groups.
3. Simultaneously with the increasing of the absorption coefficient of nanostructured WEO, change of intensity ratio of methyl and methylene groups takes place. The ratio CH_2 : CH_3 was5,2:1 in waste engine oil, but this value after nanoimpact decreases by 2,1:1. It means the amount of CH_3 qroups in nanostructured WEO, i.e.after interaction of Al_2O_3nanoparticles withwaste engine oil,increases by 2-2,5 times.

The change of intensityratio of methyl and methylene groups in nanocompositesconfirms that with entering Al_2O_3 nanoparticles into the waste engine oils nanostructuring takes place in the presented sample.It was found that with influence of small amounts of nanoparticles on waste engine oils re-groupping process took place in a certain part of hydrocarbon in WEO.As seen from spectrum4 (fig.1), with the increase of the concentration of Al_2O_3 nanoparticlesthe change of absorbtion bands'intensities corresponding to $CH_2$and CH_3groups are not observed.New characteristic bands were not found in the IR spectrum of the nanostructured WEO.However, due to the stretch vibrations of the -C = C-alkenesat 3070 cm^{-1}bandwhich characterizes alkenes, with increase of concentration of Al_2O_3 nanoparticles from 0,001 up to 1,0%,the vibration of the bands disappeared in comparison with the spectrum of initial waste engine oils.Based on the results of spectral analysis, we can conclude that when the amount of Al_2O_3nanoparticles contains more than 0,05%, the destruction process of -C=C-alkenes takes placeand the latter enters into the composition of waste engine oils.The correlation between concentration of nano Al_2O_3nanoparticles and change of absorption bands of methyl (ν_s = 2923 cm^{-1}) and methylene (ν_s= 2853 cm^{-1}) groups which enters into the composition of nanosystems confirms that the ratio of CH_2 : CH_3 reachs maximum value, when concentration of Al_2O_3 nanoparticles content is 0,001 mass.%, and by increasing concentration ofAl_2O_3 nanoparticles it decreases. This value is invariable, when concentration of Al_2O_3 nanoparticles content is 0,0001-0,01 mass.% in nanocompounds. On base of these values has been found optical dencities (fig.2).Comparative analysis of the IR spectra (figure1) and the value of D/D_0 (figure 2) of the presented samples shows that when concentration of added Al_2O_3 nanoparticles content is 0,001 mass.% nanostructuring process occursand it keeps up to 0,05 mass.% (nano Al_2O_3). The increase of concentration of Al_2O_3 nanoparticlesby 0,05% causes decrease of the -C=C-alkenes which enters into the composition of waste engine oils (initial)and then destructed completely .Thus, it was determined that optimum concentration of Al_2O_3 nanoparticles content is 0,001 mass.% and was found the impact of concentration on nanostructuring.

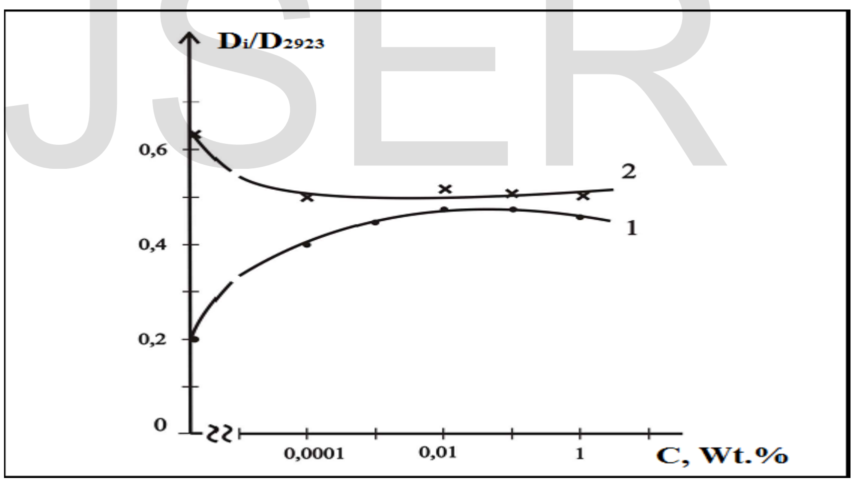

Figure 2. Dependence ofD/D_0on the amounts of Al_2O_3 nanoparticles.

Based on the analysis of the curve of the concentration dependence of the relative measurement of the optical densities of bands D2923 / D2823, was proven nanoparticle concentration effect of Al2O3. So that at low concentrations of 0.0001-0.01 wt.% nanoparticles it posses nanostructuringpropertiesbut at high concentrations 0.01-1mass.% occurs destructure . Figure 3 shows the thermograms: WEO (a) and nano -WEO (with0.001 wt% of Al2O3 nanoparticles) (b).

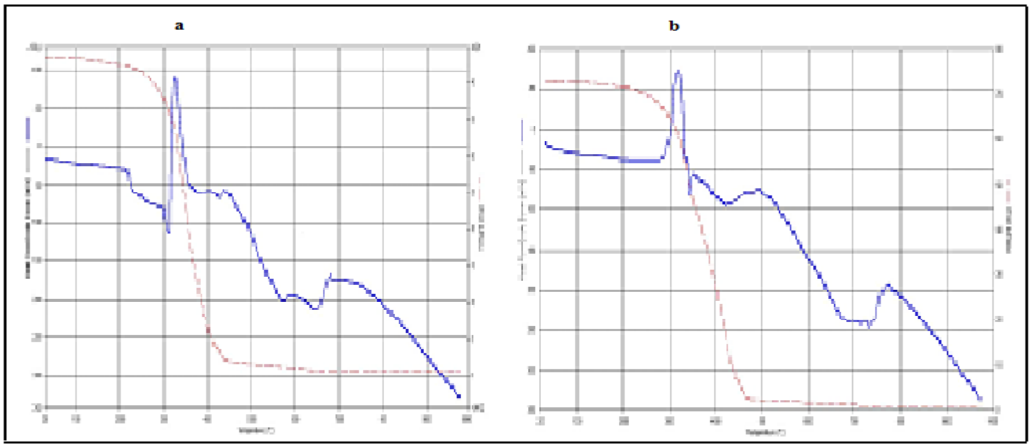

Figure 3.*Thermogramsof : a) WEO ;b) WEO +0.001 wt % of Al_2O_3 nanoparticles)*

Comparative analysis of DTQ curves (dependence of temperature onweight loss) indicated that end of complete decomposition of nano WEO (T = 450 ^{0}C) shifted toward higher temperature by 25-28^{0}C.As compared with waste engine oil (initial compound) the nanostructured composites have relatively high rheological and thermal parameters (table). This is explained by the formation of nanostructured composite, which is also proved by IR spectra.

Table. *Rheological and thermal parameters of nanocompounds on base WEO*

№	Rheological parameters	Nanocompounds : WEO + nano Al_2O_3 (mass. %)			
		0.001	0.05	0.1	1.0
1	Reduction of viscosity as compared with initial compound (%)	10-12	10-12	10-12	10-12
2	Reduction of surface tension as compared with initial compound (%)	9-10	9-10	9-10	9-10
3	Thermal parameter	0.001	0.05	0.1	1.0
4	Increasing of thermal stability as compared with initial compound (%)	18-20	18-20	18-20	18-20

CONCLUSIONS:

1. It has been obtained the nanostructured materials with new improved properties byvariation in the amount of Al_2O_3(d=20-50nm)nanoparticles impacting the waste engine oils.
2. It was determined that in initial wasteengine oilnanostructuring takes place when concentration of affectingAl_2O_3 nanoparticles is 0,0001-0,01 mass.%. When Al_2O_3 nanoparticles concentration is over 0, 05 mass.%, waste engine oils behaves as a reducing agent.
3. Addition of a small percent ofAl_2O_3 nanoparticles in the waste engine oil for using in oil industry results in performance improvement (higher thermal stability and lower viscosity).

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1.United states, Michigan,AndreBoehman - Professor, Mechanical Engineering; Director, W.E. Lay Automotive Laboratory , e-mail:boehman@umich.edu, 2045 AL (W.E. Lay Auto Lab),1231 Beal,Ann Arbor, MI 48109-2133,Phone: (734) 764-6995,**Research Interests:**Automotive engineering including: fuel production and formulation, alternative fuels, diesel combustion, spark ignition combustion, autoignition, spray behavior, particulate emissions, NOx emissions, emissions control, thermodynamics of energy conversion systems

2. US, JINHUI SONG - Ph.D. School of Materials Science and Engineering ,Georgia Institute of Technology,771 Ferst Dr. N.W., Atlanta, GA 30332,office IPST,Phone N/A,fax: 404-894-9140,e-mail: jhsong@gatech.edu

3. U.S.,M. MattiMaricq - Motor Company, MD 3179, P.O. Box 2053, Dearborn, MI, 48121, e-mail: mmaricq@ford.com (Chemistry of Diesel Fuels)