TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics and Mechanics
Vol. 55, Issue IV, 2012

MODELING AS FUNCTION OF TEMPERATURE OF VISCOSITY AND DENSITY FOR BLENDS OF DIESEL FUEL AND THERMALLY DEGRADED POLYETHYLENE

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Abstract: *The paper presents the mathematical modelling of dynamic viscosity, kinematic viscosity and density as a function of temperature for a series of binary blends between the commercial diesel fuel (CDF) and a fuel obtained by thermal degradation of Low Density Polyethylene (LDPE). The values for viscosities and density were calculated starting from the measured values for CDF and LDPE fuel as a function of temperature. The Gas Chromatography coupled with Mass Spectroscopy (GC-MS) has been used for the determination of the composition of the fuel obtained by thermal degradation of LDPE. Based on the data obtained by GC-MS the molecular weight of the fuel obtained by pyrolysis of LDPE has been calculated and the mole fraction of each component.*
Key words: *recycling, fuel, modelling, viscosity, density.*

1. INTRODUCTION

European regulators are setting increasingly stringent standards to reduce the impact of waste plastic materials (PM) on the environment. These regulations include the Directives 94/62/EC and 2005/20/EC on Waste Packaging (Romanian Government Decisions no. 349/2002 and 899/2004), the Directive 2000/53/CE on End of Life Vehicles (ELV) (Romanian Government Decision no. 2406/2004) and the Directive 2002/96/CE on Waste Electrical and Electronic Equipment [1].

Recent statistics for Western Europe estimate the annual consumption of plastic products at almost 100 kg/person for a total of over 39.1 million tons [1, 2]. This generates a vast waste stream, estimated at around 21.5 million tons/year, that needs to be effectively managed. Large quantities of all the waste plastics from Europe are still disposed of to landfill. In Romania a small quantity of plastic waste are recovered and recycling. Plastic material generates serious environmental problems due to their low density and high volume, resistance to biological degradation and combustible nature. This is the reason for intensive research for searching new and efficient methods for plastic materials recycling.

Among recycling methods, tertiary recycling leads to total depolymerization to monomers, or partial degradation to other secondary valuable materials [3] such as fuels or raw materials such as lubricating oils, synthesis gas [4].

Polyolefines contains chains formed only from carbon and hydrogen, being the most important candidates for chemical recycling for the obtaining of fuels [5]. Other plastic materials form corrosive or toxic degradation products when heated for recycling. Polyvinyl chloride (PVC) evolves corrosive hydrochloric acid (HCl) during thermal treatments applied for chemical recycling trough pyrolysis [6-9]. Polystyrene degradation conducted to a high concentration of toxic styrene. Other PM can form very toxic halogen or nitrogen containing organic compounds during tertiary recycling.

Even if the obtaining of fuels starting from polymers waste was intensively studied, research related to the properties of binary mixtures formed from diesel fuel and fuels obtained by plastic materials recycling were not approaches.

The paper presents a study related to mathematical modelling of dynamic viscosity, kinematic viscosity and density of different blends of commercial diesel fuel and LDPE derived fuel starting from the measured properties of CDF and LDPE fuels as a function of temperature.

2. EXPERIMENTAL

2.1 The obtaining of LDPE pyrolysis fuel

A bench scale installation has been used for the obtaining of fuel starting from LDPE waste. The installation is formed from a heated reactor, a cooling unit and a system for the collection of the reaction products.

Gas chromatography coupled with mass spectroscopy has been used for liquid phase analysis using a GC-MS system Agilent 7890A.

The density the dynamic and kinematic viscosity of the fuel obtained from LDPE and commercial diesel fuel (EN 590-2010) has been determined using SVM 3000 Stabinger Viscometer **(**Anton Paar), at a pressure of 974 [mbar] and a temperature of 27.6^{o}C, according to ASTM D7042. The results were presented according to ISO 3104 or ASTM D445.

2.2 The characterization of the blends of LDPE pyrolysis fuel and diesel fuel

The molecular weight of the LDPE derived fuel was calculated based on GC-MS results with the relation:

$$M = \sum \nu_i \cdot M_i \tag{1}$$

where: ν_i is the molar fraction of each identified compound and M_i is the molecular weight.

The molar fractions of the compounds (ν_i) from the oil obtained through pyrolysis have been obtained with the relation:

$$\nu_i = \frac{n_i}{n} \tag{2}$$

where: n_i is the numbers of moles of the compound i from the mixture and n is the total number of moles.

Based on the molecular weight of the diesel fuel (230 g/mole), the calculated molecular weight of LDPE oil (208 g/mole), the density (ρ) of the fuels at 20^{o}C and the volumes (V) used for blends preparation, the numbers of the moles (N) from the mixture were calculated with the relation:

$$N_{CDF} = (\rho_{CDF} \cdot V_{CDF}) / M_{CDF} \tag{3}$$

$$N_{LDPE\_F} = (\rho_{LDPE\_F} \cdot V_{LDPE\_F}) / M_{LDPE\_F} \tag{4}$$

Using the numbers of the moles (N) of the two fuels from the blend, the variation of: dynamic viscosity, cinematic viscosity and density as a function of temperature for the obtained mixture has been calculated with the relations:

Kinematic viscosity:

$$\nu_{c(t)} = \nu_{c(t),CDF} \cdot N_{CDF} + \nu_{c(t),LDPE\_F} \cdot N_{LDPE\_F} \tag{5}$$

Dynamic viscosity:

$$\nu_{d(t)} = \nu_{d(t),CDF} \cdot N_{CDF} + \nu_{d(t),LDPE\_F} \cdot N_{LDPE\_F} \tag{6}$$

Density:

$$\rho_{(t)} = \rho_{(t),CDF} \cdot N_{CDF} + \rho_{(t),LDPE\_F} \cdot N_{LDPE\_F} \tag{7}$$

tacking into account the values obtained for the pure commercial diesel fuel and the fuel obtained from LDPE (LDPE_F).

We took into consideration a series of blends, containing LDPE_F in a concentration of 5, 10, 25, 50, 70 volume % into diesel fuel.

3. RESULTS AND DISCUSSION

3.1 GC-MS analysis

Figure 1 presents the chromatogram of the low density polyethylene derived fuel and table 1 the results of chromatogram interpretation.

The obtained fuel contains saturated and unsaturated hydrocarbons with carbon numbers from 8 to 25.

One can see from table 1 that the unsaturated compounds are in smaller quantities comparing to saturated compounds. As can be seen in table 1, no aromatic compounds were identified in

LDPE fuel, leading to the conclusion that using these fuels the quantity of toxic polycyclic aromatic hydrocarbons will decrease.

Table 1

The composition, mole number and molar fraction of LDPE derived fuel determined by GC-MS

Assignment	Area %	Moles	Molar fraction
1-Octene	1.35	0.012072	0.025175
Octane	1.67	0.014594	0.030434
1-Nonene	1.15	0.009094	0.018964
Nonane	1.63	0.012754	0.026596
1-Decene	1.51	0.010786	0.022494
Decane	2.20	0.015446	0.032212
1-Undecene	2.67	0.017322	0.036124
Undecane	3.71	0.023741	0.049509
1-Dodecene	3.46	0.02056	0.042876
Dodecane	4.58	0.02692	0.056138
1-Tridecene	3.09	0.016962	0.035373
Tridecane	4.42	0.023978	0.050003
2-Tetradecene	3.34	0.017028	0.03551
Tetradecane	5.05	0.025476	0.053129
1-Pentadecene	2.95	0.014028	0.029254
Pentadecane	5.69	0.026809	0.055907
1-Hexadecene	2.53	0.011262	0.023486
Hexadecane	5.11	0.0226	0.047129
1-Heptadecene	1.68	0.007036	0.014673
Heptadecane	4.12	0.017149	0.035762
5-Octadecene	1.92	0.007625	0.015902
Octadecane	6.05	0.023774	0.049579
5-Nonadecene	1.51	0.005676	0.011838
Nonadecane	5.90	0.021989	0.045857
5-Eicosene	1.27	0.004521	0.009428
Eicosane	5.82	0.020629	0.043019
Heneicosane	5.16	0.017427	0.036343
Docosane	4.17	0.013449	0.028046
Tricosane	2.96	0.009136	0.019052
Tetracosane	2.03	0.005985	0.012481
Pentacosane	1.30	0.003695	0.007706

3.2 Fuels blends properties modelling

Starting from the calculated mole fractions (table 1) and the measured dynamic viscosity ν_d, kinematic viscosity ν_c and density ρ respectively as a function of temperature for commercial diesel fuel and low density polyethylene derived fuel, the dynamic viscosity, kinematic viscosity and density for a series of commercial diesel fuel and low density polyethylene derived fuel blends has been calculated.

The values resulted from calculations as a function of temperature have been fitted using polynomial regression for viscosity, and linear regression for density.

The dependence of measured dynamic viscosity for commercial diesel fuel and low density polyethylene derived fuel are presented in fig. 3. The dependence of dynamic viscosity as a function of temperature fit polynomial equation of third grade (table 2).

The dependence on temperature of the calculated values for dynamic viscosity of the blends are also presented in fig. 2. One can observe that the variation of calculated dynamic viscosity on temperature fit also third grade polynomial equations. The resulted equations $\nu_d = f(T)$ and the correlation factor (R^2) for the polynomial regressions are presented in table 2.

Examining table 2 and figure 2 one can see that the calculated values for dynamic viscosity in the case of the blends from commercial diesel fuel and low density polyethylene derived fuel are between the values of pure diesel fuel and low density polyethylene derived fuel.

We also observe a very high value of the correlations factors (R^2 > 0.997) for all equations.

The viscosity of the fuel obtained from LDPE is smaller than the viscosity of commercial diesel fuel and all the blends have intermediate values.

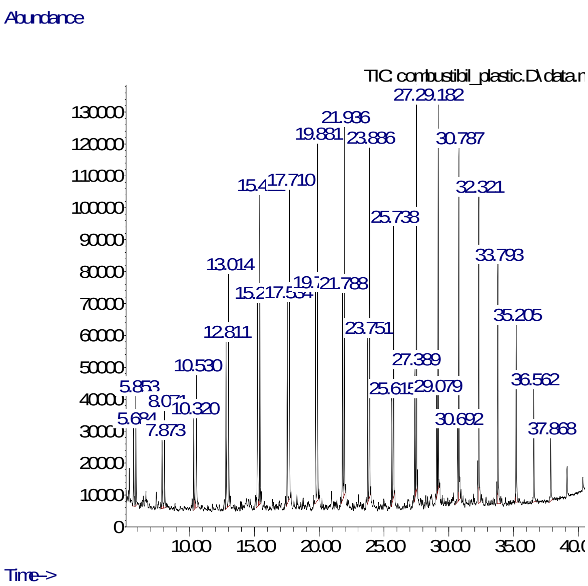

Fig. 1. Chromatogram of LDPE_F fuel

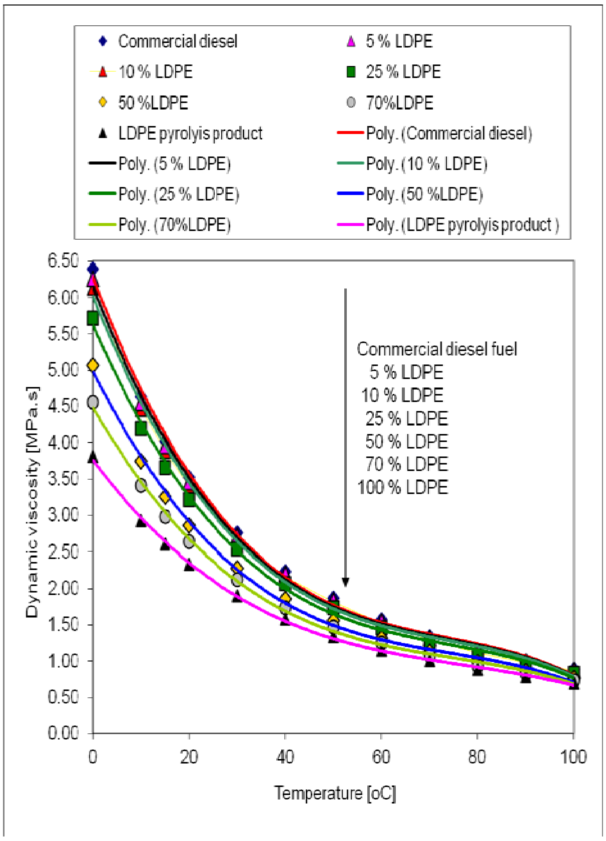

Fig. 2. The variation of dynamic viscosity on the temperature for blends formed from diesel fuel and LDPE derived fuel (measured – for pure fuels and calculated for blends)

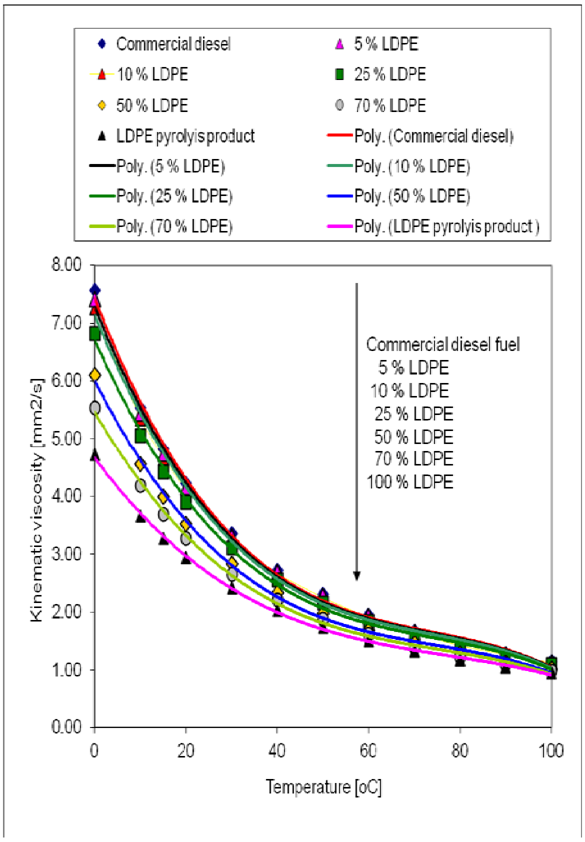

Fig. 3. The variation of kinematic viscosity on the temperature for blends formed from diesel fuel and LDPE derived fuel (measured – for pure fuels and calculated for blends)

Table 2

Polynomial equations of the variation of the dynamic viscosity as a function of temperature

Fuel	Equation	R^2
Commercial diesel fuel	y = -1E-05x3 + 0.0022x2 - 0.1747x + 6.2783	0.9977
5 % LDPE	y = -1E-05x3 + 0.0021x2 - 0.1702x + 6.1464	0.9978
10 % LDPE	y = -9E-06x3 + 0.0021x2 - 0.1657x + 6.0151	0.9978
25 % LDPE	y = -8E-06x3 + 0.0019x2 - 0.1524x + 5.6252	0.998
50 % LDPE	y = -7E-06x3 + 0.0016x2 - 0.1333x + 4.986	0.9981
70 % LDPE	y = -6E-06x3 + 0.0014x2 - 0.1158x + 4.4877	0.9984
100 % LDPE	y = -4E-06x3 + 0.001x2 - 0.0887x + 3.7595	0.999

Table 3

Polynomial equations of the variation of the kinematic viscosity as a function of temperature

Fuel	Equation	R^2
Commercial diesel fuel	y = -1E-05x3 + 0.0025x2 - 0.2022x + 7.4273	0.9978
5 % LDPE	y = -1E-05x3 + 0.0024x2 - 0.1972x + 7.2825	0.9978
10 % LDPE	y = -1E-05x3 + 0.0024x2 - 0.1922x + 7.1385	0.9979
25 % LDPE	y = -1E-05x3 + 0.0022x2 - 0.1775x + 6.7109	0.998
50 % LDPE	y = -8E-06x3 + 0.0019x2 - 0.1562x + 6.0098	0.9982
70 % LDPE	y = -7E-06x3 + 0.0016x2 - 0.1368x + 5.4632	0.9985
100 % LDPE	y = -4E-06x3 + 0.001x2 - 0.0887x + 3.7595	0.9990

Similar conclusions can be drawn for kinematic viscosity. The kinematic viscosity of low density polyethylene derived fuel is smaller than the value of commercial diesel fuel. The calculated values for the blends are intermediate between the values for commercial diesel fuel and low density polyethylene derived fuel (fig. 3 and table 3). The equations for ν_c = f(T) fit third grade polynomial regressions. The resulted equations and the values obtained for the correlation coefficient R^2 are presented in table 3.

Very high values for correlation coefficient (R^2> 0.997) can be observed from table 3 for all equations.

Density exhibits a linear variation as a function of the temperature (figure 4). The slope of the curves is 0.0007 for all samples except sample containing 70 % low density polyethylene derived fuel which is 0.0008. The intercept for the linear equations decreases with the increasing of the amount of low density polyethylene derived fuel in the blends.

The correlation factor is 1 for all curves ρ = f(t).

One can also notice that the density of low density polyethylene derived fuel is smaller than the density of commercial diesel fuel and their blends.

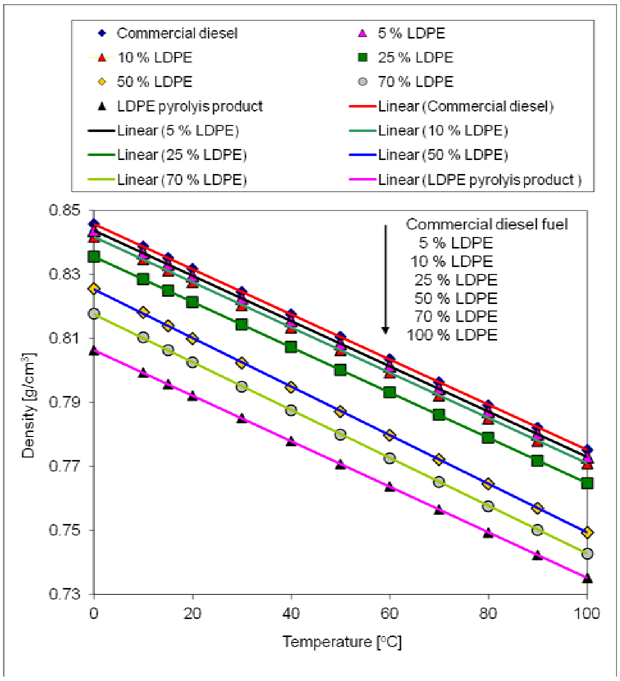

Fig. 4. The variation of density on the temperature for blends formed from diesel fuel and LDPE derived fuel (measured – for pure fuels and calculated for blends)

Table 4

Linear equations of the variation of the density as a function of temperature

Fuel	Equation	R^2
CDF	y = -0.0007x + 0.8458	1
5 % LDPE	y = -0.0007x + 0.8438	1
10 % LDPE	y = -0.0007x + 0.8417	1
25 % LDPE	y = -0.0007x + 0.8356	1
50 % LDPE	y = -0.0008x + 0.8255	1
70 % LDPE	y = -0.0007x + 0.8177	1
100 % LDPE	y = -0.0007x + 0.8065	1

The calculated values of dynamic viscosity, cinematic viscosity and density correspond to standards, leading to the conclusion that a wide range of blends could be used in internal engines.

Low density polyethylene derived fuel can be a good candidate for using in blends with commercial diesel fuels.

4. CONCLUSION

The paper presents the mathematical modelling of dynamic viscosity, kinematic viscosity and density as a function of temperature for a series of binary blends of commercial diesel fuel (CDF) and a fuel obtained by thermal degradation of Low Density Polyethylene (LDPE).

The values for viscosity and density were calculated starting from the measured values for CDF and LDPE fuel as a function of temperature.

Based on the data obtained by Gas Chromatography coupled with Mass Spectroscopy, the molecular weight of the fuel obtained by pyrolysis of LDPE and the mole fraction of each component has been calculated.

We concluded that the blends formed from CDF and LDPE fuel can be used in compression ignition engine and the studied properties (kinematic viscosity, dynamic viscosity and density) meets the demands imposed by actual legislation.

AKNOWLEDGEMENT

This paper was supported by the:
Ministry of Education, Research, Youth and Sports by the project "Proiect de dezvoltare a studiilor de doctorat în tehnologii avansate - PRODOC” contract no. POSDRU/6/1/5/S/5, project co-funded from European Social Funds through Sectorial Operational Program Human Resources 2007-2013.

Author thanks to Assoc. Prof. PhD. Eng. Istvan Barabas for viscosity and density measurements and to Researcher PhD. Eng. Adriana Gog for GC-MS analysis.

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Modelarea în funcție de temperatură a viscozității şi densității mixturilor motorinei cu polietilena degradată termic

Rezumat: *Lucrarea prezintă modelarea matematică a viscozității dinamice, viscozității cinematice şi a densității în funcție de temperatură, pentru o serie de amestecuri binare formate din motorina comercială (CDF) şi un combustibil obținut prin degradarea termică a Polietilenei de Joasă Densitate (LDPE). Valorile pentru densitate şi viscozități au fost calculate pornind de la valorile măsurate pentru CDF şi combustibilul derivat din LDPE în funcție de temperatură. S-a utilizat Cromatografia de Gaze cuplată cu Spectroscopia de masă (GC_MS) pentru determinarea compoziției combustibilului format în urma degradării termice a LDPE. Pe baza datelor obținute prin GC-MS s-a calculat masa moleculară a combustibilului obținut prin piroliza LDPE şi fracțiile molare ale fiecărui component.*

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