PHYSICOCHEMICAL PROPERTIES OF THE GASOLINE AND ALCOHOL BIOFUEL MIXTURES

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Abstract. The influence of added alcohols, ethanol and butanol, on the main biofuel properties, as the specific gravity, Reid saturated vapour pressure and distillation curves have been investigated. These properties are intimately related to the fuel composition and their prediction relies on the knowledge of its components characteristics. This research proves the possibility of obtaining fuels with different levels of resistance to detonation, using gasoline with different chemical components and various fractions of alcohols.

Keywords: alcohol, biofuel, distillation curves, gasoline, Reid saturated vapour pressure, specific gravity.

Introduction

The performance of internal combustion engines significantly depends on the physicochemical characteristics of the fuel, which in turn are determined by their chemical composition. For fuels of petroleum origin the mentioned dependencies have been studied more comprehensive than for biofuels prepared from the gasoline and monatomic alcohols. The purpose of our research has been to study the physicochemical properties and exploiting characteristics of abovementioned biofuels.

Methodology of the experimental researches

The physicochemical properties (the density, saturated vapor pressure, distillation curves, octane number etc.) as well as the exploitation characteristics of such fuels as: (a) Normal-80 gasoline brand, (b) monoatomic alcohols: ethanol C_2H_5OH (produced from sweet sorghum, must of grapes, grain, separated from ether-aldehyde fractions) and n-butanol C_4H_9OH, (c) two-component mixtures of alcohol and gasoline (ethanol-gasoline, butanol-gasoline) in proportions of: 10:90, 20:80, 30:70, 40:60 and 50:50 (% vol), (d) three-component mixtures of alcohols and gasoline (butanol-ethanol-gasoline), have been investigated. The measurements of physicochemical properties and exploitation characteristics have been performed according to the recent technical-normative documents in the Republic of Moldova.

Results and discussions

The obtained results show that the physicochemical properties and exploitation characteristics of the mixtures from alcohols (ethanol or butanol) and gasoline depend on the individual properties of alcohols, as well as on the concentration of each component in the mixture.

The crucial process that occurs in the internal combustion engine

More complete burning of the fuel combustion in engine can occur if the fuel is in a gaseous state being at the same time quite dispersed in its mixture with air. Failing to comply with this requirement makes impossible to function the engine in a good state, consequently it is very important to ensure a more complete evaporation of the fuel. The fuel capacity to move from the liquid state in the gaseous one (at certain values of pressure and temperature) represents its **volatility**, which is typically characterized by the distillation point and saturated vapor pressure.

Distillation

Under current officially authorized regulations, the beginning and end of the gasoline distillation of the "Normal-80" type is within the temperature range of 35 ÷ 215° C. The values obtained for the Normal-80 gasoline sample, taken as the base for subsequent mixtures, are within the range of 42 ÷ 194° C (Table 1).

Table 1

The main characteristics of studied fuels

Fuel characteristics	Values of fuel characteristics								
	Gasoline N-80 (really obtained/ norm of SM 226)	**Butanol (N-butane) B 100**	**B 10**	**B20**	**E 20 Rect. ethanol**	**E 20 EAF Ethanol**	**EAF Ethanol E 100**	**E18B10**	**E16B16**
Distillation:									
- initial temperature of distillation, ºC	42/>35*	110	43	40	40	40	76	38	43
-temperature of distillation, ºC:									
10% vol.	55/<75*	113	55	52	47	48	77	46	53
50% vol.	85/<120*	116	87	89	67	67	78	70	84
90% vol.	154/<190*	116	154	147	143	145	83	131	120
-Final point of distillation, ºC	194/<215*	116	194	192	193	192	95	191	193
-Residue, % vol.	1.3 / <2*	1.0	1.2	1.2	1.1	1.2	0.1	1.3	1.4
-Residue + lost, % vol.	2.5 / <4*	2.0	2.5	2.0	2.0	2.0	0.5	2.0	2.0
Motor octane number MON	75.5	86.5	77.3	78.8	84.8	84.9	91*	84.7	84.6
Density. (20˚C). kg/m^3	728/<775*	797	733	739	745	745	806/ 790*	742	750
Cinematic viscosity (20˚C). mm^2/s	0.57	3.64	0.65	0.73	0.76	0.69	1.52	0.81	0.91
Saturated vapor pressure. kPa	54.3/<80*	4	50.9	47.5	61.2	58.7	23*	54.8	50.9

* According to the normative or informative data; Rect. ethanol - Rectified ethanol, Ethanol EAF - ether-aldehyde fraction of ethanol

By the chromatographic analysis it has established that ethanol, made from the sweet sorghum and used to prepare combustible mixtures, contains 96 - 98% vol. of ethanol, up to 0.1% vol. of methanol and up to 1.4% of the ether-aldehyde fraction, the remaining part (2-3%) being water. In addition it also contains up to 3 g/L of the fusel oil and 0.3 g/L volatile acids.

The initial point of distillation of the gasoline must be not lower than +35°C in order to minimize the loss of light hydrocarbons during the transportation and storage. The values of the initial point of distillation for ethanol-gasoline mixtures increase by 2-6ºC (ethanol = 5-40% vol.) in comparison with the usual changes within the range of 38 - 42°C. The increase of the initial point of distillation for biofuels (ethanol-gasoline mixtures) is determined by the presence of ethanol, whose distillation temperature is 76ºC. In function of the volume fraction of added ethanol, the temperature increases by 2-6°C, being at the level of 38-42°C. From the obtained data one can conclude that the addition of ethanol up to 40-50% vol. conducts to an increase of the initial point of distillation t_{init} for biofuels, so the t_{init} value is established within the range of 38-44°C. The influence of butanol on the values of the initial point of distillation is similar as for ethanol, but still lower, because the polarity of butanol is closer to that of gasoline and, although the distillation temperature of butanol (110°C) is much higher, the addition of butanol does not practically change the respective temperature for the binary mixture (t_{init} varies between 40 and 43ºC) as well as for the ternary mixture of biofuels (t_{init} varies between 38 and 43ºC).

The distillation temperature of 10% vol. is important for the starting capacity of the engine: the temperature is lower, the better are the starting conditions. Although the distillation temperature of 10% vol. of ethanol (t_{10} =77ºC) is higher than that of gasoline A-80 (t_{10}= 55ºC), the presence of ethanol in biofuels with the volume fraction up to 20% decreases the t_{10} value by 1-8°C. The common feature for all ethanol-gasoline blends is the fact that the distillation temperature increases as the ethanol concentration grows. For the ethanol concentrations above 20% vol., the t_{10} value for biofuel exceeds the respective temperature of gasoline by 1-8°C. Regardless of the composition and properties of studied biofuels, an addition up to 20% vol. of ethanol stabilizes the t_{10} value of biofuels within the range of 47-52°C, while with the ethanol concentration increasing up to 50% vol. - within the range of t_{10}= 52 °C -59 °C. The distillation temperature t_{10} of butanol (113°C) is much higher than that of gasoline (55ºC). At the same time, the t_{10} value for the butanol-gasoline mixture (55°C for $C_{butanol}$=10% vol., 52ºC for $C_{butanol}$=20% vol.) is by 1-3°C lower than that of gasoline. This may be explained by molecular interactions, but with a less effect than that for ethanol-gasoline mixtures. The addition of butanol to the ternary mixture E18B10 in proportion of 10% vol. maintains the t_{10} value at 46°C, while for the ratio of 20% vol. the t_{10} value increases up to 53°C.

The distillation temperature of 50% vol. characterizes the fuel capacity to ensure a proper functioning of the engine at different loads and especially in the case of their variation. The excellent function of the spark ignition engine (SIE) is guaranteed when the t_{50} value of gasoline is below 120ºC. In the case of A-80 gasoline, the distillation temperature of 50% vol. is 85°C, while for ethanol is 78°C and for butanol is 116°C. The addition of butanol (10-20% vol.) increases by 2-4°C the t_{50} value when mixed with gasoline and by 3-17ºC in the ternary mixture. In the latter case the largest increase (17°C) occurs at the butanol concentration of 20% vol. in the E16B16 mixture. For the t_{50} value, the synergic influence of butanol is minimal and with increasing the concentration of butanol, especially in the biofuel mixtures, the temperature t_{50} increases substantially, near to that of the gasoline A-80.

The distillation temperature of 90% vol. and the distillation end point describes the complete combustion capacity and the fuel efficiency. For the A-80 gasoline the t_{90} value is equal to 154°C, for ethanol is of 83°C, and for butanol is 116°C. The increase of the ethanol volume fraction up to 30% results in maintaining or lowering the t_{90} value by maximum 11ºC compared to gasoline. The increase of the ethanol volume fraction by more than 30% leads to a more pronounced decrease in the t_{90} value. Thus, for the biofuel E50 the t_{90} value is of 87°C, the decrease being of 72ºC. In the butanol mixtures the decrease of temperature takes also place: in the gasoline blends of up to 7ºC, while in the ternary mixtures up to 34ºC (see table 1).

The distillation endpoint of studied gasoline varies within the range 177-194°C. The addition of alcohol decreases by up to 12ºC the final point of distillation of the ethanol blends and up to 3°C for mixtures with butanol. In both cases this decrease becomes more pronounced with increasing the volume fraction of alcohols in the mixture.
According to [13], the temperature range $\Delta t = t_{final} - t_{90}$ decreasing reflects the diminish of probability of the condensation for heavy fractions of fuel. This range is, respectively: for gasoline A-76, Δt = 18°C; for A-80, Δt = 39-40°C, for ethanol, Δt = 12°C and for butanol, Δt = 0ºC. The addition of ethanol and butanol in the ratio of up to 30-40% vol. changes the temperature difference Δt for the respective gasoline within relative small range: ± 8°C. With increasing the alcohol fraction over 40% vol., the difference Δt increases to 79°C, mostly due the t_{90} value decreasing.

The residue is a non-distilled fraction of fuel, formed from its heavy fractions. The residues remained after the distillation of ethanol (0.1% vol.) and butanol (1.0% vol.) are smaller than those for the respective gasoline (1.3% vol.). In the binary mixtures of ethanol-gasoline and butanol-gasoline there is registered a slight decrease of the residue compared with gasoline of the 0.6 - 1.2% vol. levels.

Distillation losses were 1.2% vol. for gasoline, respectively 0.4% and 1.0% vol. for ethanol and butanol.

The fractional composition (distillation) is reflected by the distillation curves (fig. 1). In the temperature range of t_{init}-t_{10} the distillation of biofuels (except E50) is practically identical to that of gasoline. The use of ethanol produced from various species of raw material (as sorghum mellitus, ether-aldehyde fraction of grapes or grain) does not essentially influence the distillation temperatures of biofuels. The form of distillation curves shows that the addition of ethanol and butanol to gasoline influences insignificantly on the initial and final distillation point values of mixed fuels, but there is a certain decrease in the intermediate distillation temperatures (t_{10}, t_{50}, t_{90}) for the mixtures of monatomic alcohol and gasoline.

The vapor pressure also influences on the proper engine function. The Reid vapor pressure of the gasoline A-80 is equal to 54.3 kPa, while that for gasoline with the ethanol fraction of 10% vol. and 20% vol. is situated within the 57.0 - 61.2 kPa range. The tendency of increasing pressure with growing the ethanol volume fraction has been registered. Since the vapor pressure of butanol is low (4 kPa), its addition to gasoline with the volume fraction of 10% and 20% reduces the pressure of the A-80 gasoline respectively by 3.4 kPa and 6.8 kPa, while for the biofuel E16B16 respectively by 6.4 and 10.3 kPa.

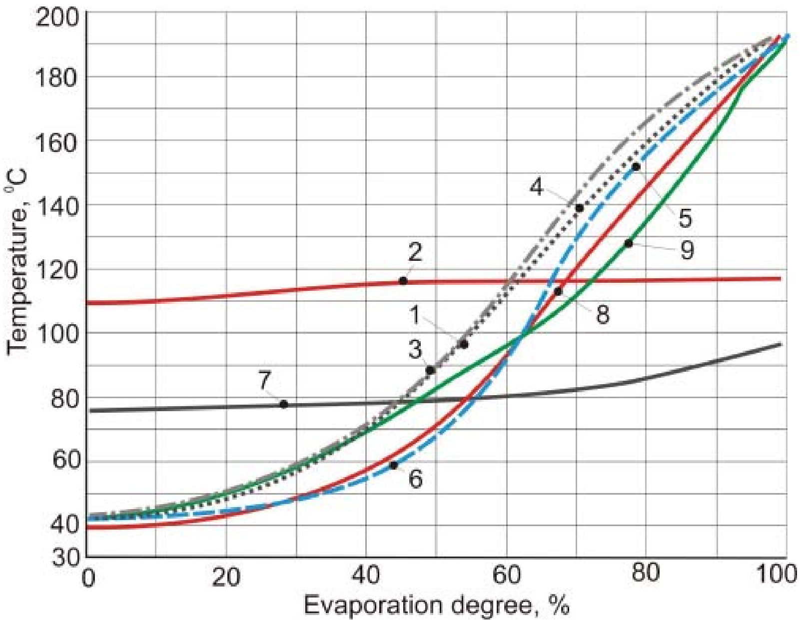

Fig. 1. Modification of the fuel distillation curves: 1 - gasoline A-80, 2 - butanol, 3 - ethanol, 4 - B20 mixture, 5 - biofuel E20 (rectificated) 6 - biofuel E-20 (EAF), 7 - ethanol, 8 - E18B10 mixture, 9-E16B16 mixture

Octane number characterizes the detonation stability and is determined by the Research Method (RON) or Motor Method (MON). It has been established that adding alcohol to gasoline usually increases the octane number (fig. 2). The addition of ethanol causes a higher increase of the octane number (ΔCOM = 0.47 unit /% vol.) than in the case of butanol (ΔCOM = 0.17 unit /% vol.).

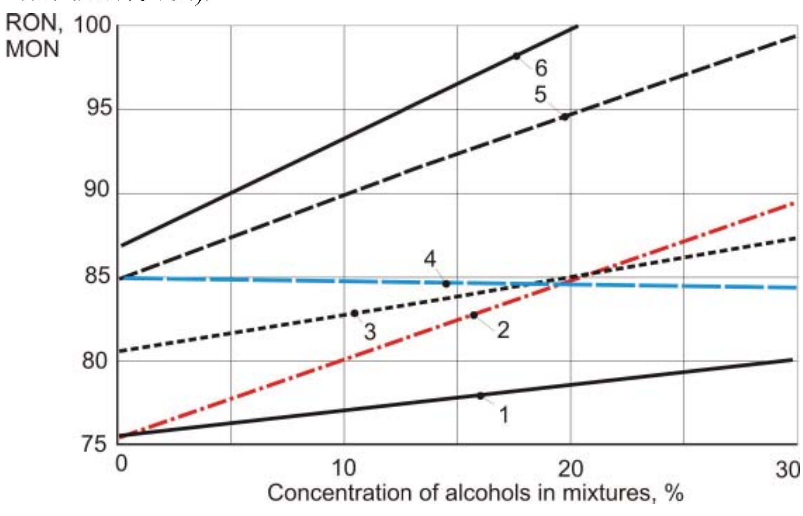

Fig. 2. The dependence of the octane number of biofuel mixtures on the alcohol concentrations: 1, 2, 3, 4 - COM = f (C), 5, 6 - COR = f (C), 1 - butanol + gasoline A-80, 2 - ethanol + gasoline A-76, 3 - ethanol + gasoline A-80, 4 - E16B16 mixture, 5 - ethanol + gasoline A-80, 6 - ethanol + gasoline A-90

Conclusions

1. It has been established that adding ethanol to 40 - 50% vol. has a positive effect on the initial distillation temperature values for biofuels, which are stabilized in a range t_{init} 38 - 44˚C. The influence of butanol on the initial distillation temperature values is identical to that of ethanol. Even the distillation temperature of butanol (t_{init}= 110˚C) is much higher than that for gasoline (t_{init}= 42˚C), adding butanol does not practically change the respective temperature of the binary mixture with gasoline (t_{init}= 40 - 43˚C) as well as for ternary mixture of biofuel (t_{init}= 38 - 43˚C).

2. The addition of alcohols with up to 20% volume fraction in gasoline creates a synergistic effect, reducing that the temperature by 1 - 8˚C. At addition of butanol this effect is lower than for ethanol. The increase of the ethanol content more than 20% vol. results in growing the t_{10} value of biofuel by 1 - 8˚C. The best fuels to start the engine are the mixtures that contain alcohols up to 20 - 30% vol.

3. The ethanol-gasoline blends E5-E50 (with the ethanol fraction of 5 - 50% vol.) have the t_{50} value within 67 - 79˚C, for gasoline - t_{50} = 85 - 95˚C and for ethanol t_{50}=78˚C.. Reducing the temperature t_{50} for biofuel, especially with the ethanol concentration up to 30% vol., has to improve the engine performance at different tasks and is caused by the interaction of component molecules with a synergistic effect. The addition up to 20% vol. of butanol (t_{50} = 116˚C) increases by 2 - 4˚C the temperature t_{50} in the mixture with gasoline and by 3 - 17˚C in the mixture with the biofuel.

4. The alcohols have the temperature t_{90} lower than gasoline (t_{90}= 152 - 159˚C), so for the alcohol-gasoline fuel blends, the 90% distillation temperature has low values. The distillation endpoint drops to 12˚C in the ethanol-gasoline blends and with up to 3˚C in the butanol-gasoline mixtures. The reduction of t_{90} and t_{final} leads to the more complete burning of fuel.

5. The distillation curves show that the addition of monoatomic alcohols in gasoline affects slightly the initial and final points of distillation of mixed fuels, but there is a certain decrease in the intermediate distillation temperature (t_{90}, t_{90}, t_{90}) of the mixtures of alcohols with gasoline.

6. The Reid saturated vapor pressure RVP of studied fuels does not exceed the current normative requirements and technical documents (RVP < 80 kPa). The vapor pressure of the A-80 gasoline is within 49 - 54.3 kPa while that of biofuels with the volumetric fraction of 10% ethanol and 20% vol. is respectively within 57 - 61.2 kPa. The addition of butanol (RVP 4kPa) with the volume fraction 10% and 20% decreases RPV in gasoline by 3.4 and 6.8 kPa respectively, while for the biofuel E20 by 6.4 and 10.3 kPa correspondingly.

7. The addition of ethanol to gasoline (MON 75.5) provides a higher octane number growth (ΔMON = 0.47 unit\% vol.) than in the case of the addition of butanol (ΔMON unit = 0.17 unit\% vol). Under the same conditions, the addition of alcohols leads to an increase in the Research Octane Number higher than for the MON. The addition of up to 20% vol. of butanol does not practically influence the resistance to the detonation of the biofuel E20 (MON 84.8 - 84.6).

8. The carried out research proves the possibility of obtaining fuels with different levels of resistance to detonation, using gasoline with different chemical components and various fractions of alcohol.

Acknowledgments. This work was supported by the "Development and use of the optimized compositions of biofuel mixtures based on physico-chemical modeling" 5393A STCU research project funding.

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