

H₂O removal from diesel and JP8 fuels: A comparison study between synthetic and natural dehydration agents

E. P. Favvas^{1,*}, C. G. Tsanaksidis², G. T. Tzilantonis² and S. G. Christidis²

¹Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi, Attica, 153 41, Greece

²Department of Pollution Control and Technologies, Technological Education Institute of Western Macedonia, Kila, Kozani, 501 00, Greece

Received 8 April 2014; Accepted 11 August 2014

Abstract

The comparison between Thermal Polyaspartate Anion, TPA, and natural resin in their effect on the improvement of the physicochemical properties of both conventional diesel and JP8 fuels is the main scope of this work. Specifically, both studied materials were used dehydration agents in order to increase the physicochemical properties of both treated fuels. The higher amount of the removed water was obtained when used the natural resin as adsorbent material. In this case the water concentration decreased into diesel up to 68.66 % and more than 30 % in the case of jet fuel (JP8). This water removal improves the studied physicochemical properties of both studied fuels, diesel and JP8, for example up to 633 J/g (using natural resin as dehydration agent (*removable additive*)) and 1040 J/g (using TPA as dehydration agent) for the heat of combustion. Overall, the proposed method can be used in a simple fuel cleaning process using a metal mesh vessel of synthetic TPA polymer or natural resin. The higher water/humidity removal amount in conjunction with the very low price of the natural resin makes this material more promising for the up scaling of the proposed technique in the near future.

Keywords: Water removal, diesel and JP8 fuels, dehydration agents, TPA, natural resin.

1. Introduction

Petroleum, natural gas, coal, renewable sources and nuclear technology are the most important energy sources worldwide. Based on the last report, October 2013, of the U.S. Energy Information Administration (EIA), a principal agency of the U.S. Federal Statistical System and part of the U.S. Department of Energy, the Primary Energy Consumption follows the bellow ranking (the values in parenthesis are in Quadrillion Btu): petroleum (3.022) – natural gas (1.949), coal (1.727), renewable energy (0.804) – nuclear electrical power (0.738) [1]. This classification of the energy sources seems to be stable for the next decades and this is a major reason in order to develop new technologies for the quality improvement and the environmental impact of the conventional, mineral, fuels. To this end standard values for each physicochemical parameter are established in order to keep the fuel quality in high levels and both engines and environment protected. The quality of automotive fuels in the European Union is specified by standards developed by the European Committee for Standardization (CEN). The first set of CEN-ratified standards (March 1993) for automotive fuels was adopted by all member states in September 1993. Three standards cover automotive fuels quality: the EN 590 for diesel fuel, the EN 228 for gasoline and EN 589 for automotive LPG. The

standards are periodically updated to reflect changes in specifications, such as the mandatory reductions in sulfur content [2]. The low combustion efficiency and the high pollutant contents of liquid hydrocarbon fuels (gasoline, diesel fuel and jet fuels) are also responsible for the air pollution and as a result, many studies have focused on the improvement of diesel or/and blend fuel's properties [3–7].

The majority of these applied technologies, which are used for the increase of the fuel properties, are based on the use of additives. A big category of these additives is the metal compounds which can improve, for instance, the diesel properties of freezing point and cetane number. Metin Gürü et al. [8] reported that when used as additives organic compounds of Manganese (Mn), Magnesium (Mg), Copper (Cu) and Calcium (Ca) metals, these additives reduced the freezing point to 12.4 °C at the rate of dosage of 54.2 µmol Mn/L Diesel fuel. It was also established that the cetane number of Diesel fuel without the additive was 46.22, whereas the cetane number was 48.24 for Diesel fuel with the optimum amount of dosage. Fazliakmetov and Shpiro [9] reported that particulate matter (PM) emission is reduced when Iron (Fe), Manganese (Mn), Cerium (Ce) content additives are used for Diesel engines. In another work by Eliana W. de Menezes and coworkers [10] was reported the effect of ether additives ((Ethyl Tertiary Butyl Ether (ETBE) and Tertiary Amyl Ethyl Ether (TAEE)) on diesel and of ether/ethanol/diesel blends. Specifically properties such as density, volatility, viscosity, and characteristics at cold temperatures, the cetane number and the performance in engine tests were studied and reported. The results indicate

* E-mail address: favvas@chem.demokritos.gr

that the presence of ethanol and ETBE significantly alter the characteristics of volatility (flashpoint and distillation curve) and reduce the cetane number, impairing the fuel's performance in engine tests. The last decade the interest of the scientific community has shifted from the area of the conventional diesel fuel to the area of biofuels based fuels, especially in these which are commercialized. For example an "update" of the E. W. de Menezes' work comes in 2011 when D.H. Qi and coworkers reported the effect of diethyl ether and ethanol additives on the combustion and emission characteristics not of conventional diesel but of biodiesel-diesel blends fuels [11]. They conclude that Biodiesel/diethyl ether/diesel blend (BE-1) and biodiesel/ethanol/diesel blend (BE-2) show better stability and can be used in diesel engine without any modification.

In this work a comparison between two hydrophilic polymers in their ability to adsorb water from conventional fuels is reported. Specifically, the improvement of the physicochemical properties, in diesel and JP8 fuel (jet fuel), was obtained using the thermal polyaspartate anion [3], a derivative biopolymer of aspartic acid, as dehydration agents (removable fuel additive) as well as by a natural resin from *Pinus halepensis* trees [12]. The effect of these two water adsorbents on a series of the physicochemical properties of the studied fuels was studied and presented. Except for the water concentration (water solubility saturation level), properties such as the heat of combustion, the flash point, the conductivity, the kinematic viscosity, the density etc were measured and discussed according to the ASTM standard methods.

2. Experimental

Thermal Polyaspartate Anion (Fig. 1), a derivative biopolymer of aspartic acid, was used in order to remove water residues of both diesel and JP8. Thermal Polyaspartate Anion is a biopolymer synthesized from aspartic acid, a natural amino acid [3,13,14]. The TPA polymer was synthesized from our group and its synthesis route is described previously [3].

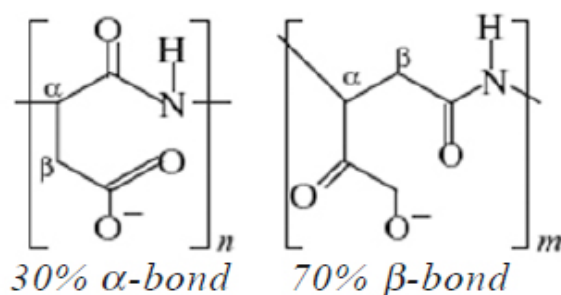


Fig. 1. Thermal Polyaspartate Anion (TPA).

In addition, natural resin (Fig. 2) a natural product from *Pinus halepensis* trees, was also used in order to remove water residues from diesel and JP8 fuels. The natural resin used was collected from the forests of North Greece region and was used as dehydration agents (removable additive) after a simple purification [11]. This natural resin is a mixture of monoterpenes (32.9 %), sesquiterpenes (1.26 %) and diterpenes (65.84 %) [12].

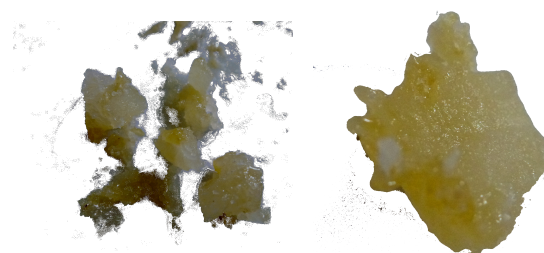


Fig. 2. Pictures of Natural Resin.

In order to investigate the effect of these two materials, the hydrophilic polymers, a contrast mass amounts of TPA and natural resin were blended in numerous diesel and JP8 samples and the change of water amount was recorded with time. During the mechanical mixing of the additive and the fuel both liquid volume and polymer mass were kept constant [3,12]. Based on this procedure a numerous of important physicochemical properties were measured before and after the treatment with hydrophilic removable additives (dehydration agents) and the results are presented and discussed.

Note that the water removal from the fuel samples, diesel and jet fuel (JP8), was the main target of this process and as the results shows this was achieved in a good efficiency by using the both materials. Furthermore, the natural resin was recorded as better water amount adsorbent a phenomenon which has studied separately in our previous work [3] where the capacity of the adsorbed pure water was measured up to 0.0018 g water/g resin by isotherm adsorption measurement. The separate study of water adsorption isotherm and their kinetics characteristics of the thermal polyaspartate anion is a study which is scheduled for the near future.

3. Results and Discussion

3.1. Diesel

In general diesel fuel is any liquid fuel used in diesel engine. Specifically, petroleum-derived diesel is increasingly called petrodiesel [15]. Diesel fuel is widely used in most types of transportation, mainly in automotive both for private and commercial uses [16]. Due to this extremely large consumption of diesel fuel the necessity for the development of new technologies for the improvement of the physicochemical properties of diesel is now quite crucial. To this end our contribution focused on the development of a new method which presents good results with low cost and without any environmental repercussion.

In both cases, where TPA as well as natural resin was used as additive, the hydrophilic polymer was just blended, mechanically, with the diesel. After same time of mixing the hydrophilic polymer was removed from the fuel. From the same batch of diesel sample different "snapshots" were prepared and studied as a function of the additive concentration and blending time. The interesting physicochemical properties of the diesel were measured before and after the applied treatment. In particular the specific ASTM methods were used for the determination of the measured properties: density (at 15 °C, g/mL) [17], kinematic viscosity at 40 °C (cSt) [18], water amount (mg water/kg fuel (ppm(m))) [19], heat of combustion (J/g) [20], total acid number (mg KOH/g) [21] and cetane index (C.I.) [22]. Note that the used commercial diesel sample was into

the limits of the standard values, according to the Greek and European Specifications for Diesel Fuels. All these properties of the studied diesel samples were improved after the treatment with the TPA and natural resin.

In specific, the density was decreased by 0.24 and 0.72 %, the kinematic viscosity by 0 and 1.26 %, the water amount by 39.4 and 68.7 %, the heat of combustion by 463 and 633 J/g, the total acid number by 28.23 and 12.64 % and the cetane index by 6.15 and 4.34 % in cases where used as dehydration agents (removable additives) the TPA and the natural resin respectively. These differences of the degree (%) of the changes of the mentioned studied properties are shown in Fig. 3.

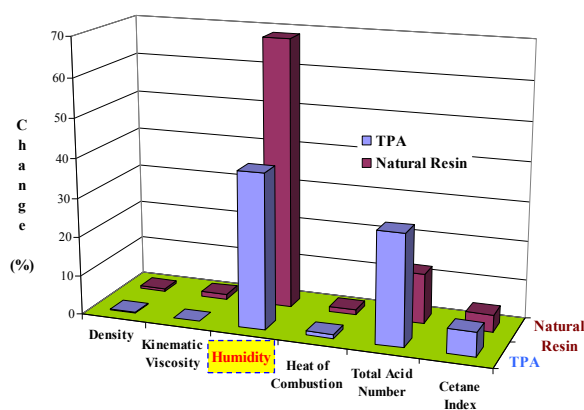


Fig. 3. Comparison between the effect of TPA and Natural Resin dehydration agents in the degree of improvement of a numerous of physicochemical studied properties for commercial, conventional diesel fuel.

As we can see from the Fig. 3 the higher water removal efficiency was obtained when it was chosen as adsorbent material the natural resin and not the synthetic thermal polyaspartate anion. This achievement obtained thanks to the higher water adsorption properties of the natural resin with reference to the synthetic TPA polymer.

On the other hand the TPA seems more effective material only in the cases of the improvement of the total acid number and cetane index of the diesel samples.

Table 1. Physicochemical properties of pre-treatment and after treatment (with TPA and natural resin) diesel fuel.

Property	"Raw" diesel	After Treatment With TPA	"Raw" diesel	After Treatment With Natural Resin
Density (g/mL)	0.826	0.824	0.833	0.827
Water concentration (mg water / Kg diesel)	107.4	65.1	157.3	49.3
Heat of Combustion (J/g)	44049	44512	46126	46759
Total Acid Number (mg KOH/g)	0.085	0.061	NA	0.087
Cetane Index	51.4	54.56	53.0	55.3

Finally all these reported properties, the density, the Water amount, the Heat of Combustion, the Total Acid Number and the Cetane Index, are presented in Table 1 in the cases of pretreatment diesel and after the treatment with TPA and natural resin hydrophilic properties.

3.2. Jet Fuel (JP8)

The light jet fuels such as Jet A-1 fuel (kerosene, a "wide-cut" jet fuel) can be produced by the straight distillation from crude oil or during catalytic processes from residues distillation of products. The JP8 fuel was enriched using antioxidants, dispersants or corrosion inhibitors as additives [5]. Jet fuels come from the mixture of petroleum hydrocarbons, mainly based on methane hydrocarbons series, consist of 10 to 16 carbon atoms per molecule. A typical composition of this fuel types depends on paraffins (n-, iso-, monocycle-, bicycle- and tricycle-), olefins, aromatics hydrocarbons, nitrogen as well as sulfur impurities [3]. The low combustion efficiency and the high pollutant contents of liquid jet fuels are also responsible for the air pollution and the toxicological effects [23]. The fuel purity is a major characteristic which is responsible for their thermal stability as well as for all the characteristics of physicochemical properties. The knowledge of the concentration of contaminations, such as water and sulfur components, is important for evaluating fuel quality and behavior during the combustion [24–26].

Especially, the "disappearance" of any water trace is a major target because the ice formation at low temperatures results in fuel flow blockages and is a major problem especially in the case of jet fuels [3]. This solute water can also cause major problems such as metal corrosion and microbial growth in engine equipments and fuel tanks [26,27]. A very interest study of the ice growth in aviation jet fuel is reported by Joseph K.-W. Lam and coworkers [28]. These ice particles, exhibiting 1h polymorph characteristics, were found to nucleate and grow on surfaces at sub-zero temperatures. A recent, similar to our work, paper which describes a systematic approach towards the development of jet fuel additives which are kinetically fast, selective, lipophilic water scavengers that produce, upon hydrolysis, a hydrophilic ice inhibitor comes from S. Repetto and coworkers [29].

By the same way with the case of diesel fuel both TPA and natural resin were used as dehydration agents (removable additives) in JP8. The hydrophilic polymers were just blended (sequentially), mechanically with the JP8 and after several mixing times were removed from this. From the same batch of JP8 sample different "snapshots" were prepared and studied as a function of the additive concentration and blending time.

The interesting physicochemical properties of the JP8 were measured before and after the applied treatment. In particular the specific ASTM methods were used for the determination of the measured properties: density (at 15 °C, g/mL) [17], water amount (mg water/kg fuel (ppm(m))) [19], heat of combustion (J/g) [20] and flash point (°C) [30].

The used commercial JP8 was into the limits, according to the Greek and European Specifications for JP8, also before the treatment with the two removable polymers.

The treated samples of the JP8 presented changed their physicochemical properties in both cases of the used water adsorbent materials. All these properties of the studied JP8 samples were changed after the treatment with the TPA and natural resin. In specific, the density was decreased at 0.25

and 0.9 %, the flash point at 6.15 and 2.15 %, the heat of combustion at 1040 and 187 J/g and finally the water amount at 26 and more than 30 % in the cases where the TPA and the natural resin were used as dehydration agents (removable additives) respectively.

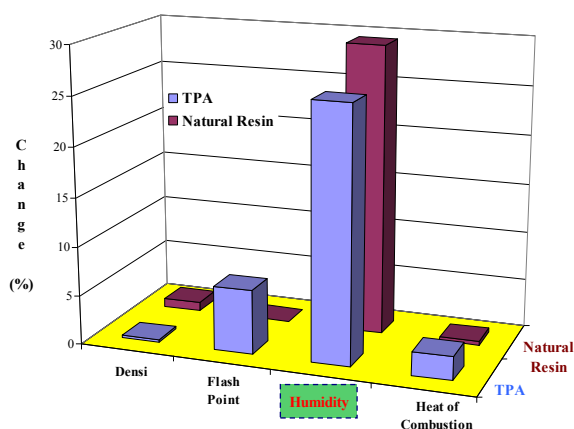


Fig. 4. Comparison between the effect of TPA and Natural Resin dehydration agents in the degree of improvement of a numerous of physicochemical studied properties for commercial, conventional JP8 fuel.

These differences of the degree (%) of change of the mentioned studied properties are shown in Fig. 4. Finally all these reported properties, The density, The Water amount, the Heat of Combustion, the Total Acid Number and the Cetane Index, are presented in Table 2 in the cases of pretreatment JP8 fuel and after the treatment with TPA and natural resin hydrophilic properties.

Table 2. Physicochemical properties of pre-treatment and after treatment (with TPA and natural resin) JP8 fuel.

Property	"Raw" JP8	After Treatment With TPA	"Raw" JP8	After Treatment With Natural Resin
Density (g/mL)	0.797	0.795	0.80	0.79
Water concentration (mg water / Kg JP8)	57.1	42.4	68	<50
Heat of Combustion (J/g)	43520	44560	46167	46354
Flash Point (°C)	46	49	46.5	45.5

4. Conclusion

The present study was an attempt to compare the differences of the effect of two hydrophilic polymers in the proposed method for the improvement of the diesel and JP8 physicochemical properties. Both thermal polyaspartate anion (TPA) and natural resin, from pine trees, were used as a water/humidity adsorbent in order to purify diesel and JP8 fuels. The higher amount of the water removal was obtained when the natural resin was used as dehydration agents (removable additive). Specifically, when the TPA was used as dehydration agents, the water amount decreased up to 39.4 and 25.7 % for diesel and JP8 respectively whereas when the natural resin was chosen as dehydration agents the water amount decreased up to 68.7 and more than 30 % for diesel and JP8 respectively. Except for the decrease of the water, the physicochemical properties of density, kinematic viscosity, flash point and heat of combustion, of both studied fuels, were changed, mostly improved, after the treatment with the TPA and natural resin.

References

- [1] U.S. Energy Information Administration (EIA), Monthly Energy Review. July 2013, <http://www.eia.gov>.
- [2] European Committee for Standardization, <http://www.cen.eu/cen/pages/default.aspx>.
- [3] C.G. Tsanaksidis, S.G. Christidis and E.P. Favvas, "A novel method for improving the physicochemical properties of diesel and jet fuel using polyaspartate polymer additives," *Fuel* **104**, 155 (2013).
- [4] C.G. Tsanaksidis, S.G. Christidis, N. Sariannidis and A. Itziou, "Regression analysis about humidity elimination and reduction conductivity from JP8 via a hydrophilic polymer," *Petroleum Chemistry* **52**, 447 (2012).
- [5] C. Song, "An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel," *Catalysis Today* **86**, 211 (2003).
- [6] R.C. Santana, P.T. Do, M. Santikunaporn, W.E. Alvarez, J.D. Taylor, E.L. Sughrue and D.E. Resasco, "Evaluation of different reaction strategies for the improvement of cetane number in diesel fuels," *Fuel* **85**, 643 (2006).
- [7] C.G. Tsanaksidis, E.P. Favvas, G.T. Tzilantonis, A.V. Scaltsoyiannes, "A new fuel (D-BD-J) from the blending of conventional diesel, biodiesel and JP8," *Fuel Proc. Technol.* **127**, 66 (2014).
- [8] M. Gürtü, U. Karakaya, D. Altıparmak and A. Alıcılar, "Improvement of Diesel fuel properties by using additives," *Energy Convers Management* **43**, 1021 (2002).
- [9] R.G. Fazliakmetov and G.S. Shpiro, "Selection and manufacture technology of antismoke additives for diesel fuel and boiler fuels oils," *Izdetal. Stvo Neft. I. Gaz.* **4**, 43 (1995).
- [10] E.W. Menezes, R. Silva, R. Cataluña and R.J.C. Ortega, "Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests," *Fuel* **85**, 815 (2006).
- [11] D.H. Qi, H. Chen, L.M. Geng and Y.Z. Bian, "Effect of diethyl ether and ethanol additives on the combustion and emission characteristics of biodiesel-diesel blended fuel engine," *Renewable Energy* **36**, 1252 (2011).
- [12] C.G. Tsanaksidis, E.P. Favvas, A.A. Scaltsoyiannes, S.G. Christidis, E.X. Katsidi and A.V. Scaltsoyiannes, "Natural resins and their application in antifouling fuel technology Part I: Improving the physicochemical properties of diesel fuel using natural resin polymer as a removable additive," *Fuel Proc. Technol.* **114**, 135 (2013).
- [13] A.P. Wheeler and L.P. Koskan, "Large scale thermally synthesized polyaspartate as a substitute in polymer applications," *Mater. Res. Soc. Symp. Proceed.* **292**, 277 (1993).

- [14] K.C. Low, A.P. Wheeler and L.P. Koskan, "Commercial poly (aspartic acid) and its uses. Advances in chemistry series," American Chemical Society. Washington-DC (1996).
- [15] G. Knothe, C.A. Sharp and T.W. Ryan, "Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine," *Energy and Fuels* **20**, 403 (2006).
- [16] The World Bank,
<http://data.worldbank.org/indicator/IS.ROD.DESL.PC>
- [17] ASTM D1298-99 (2005) Standard Test Method for Density Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method.
- [18] ASTM D445-06 (2006) Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity).
- [19] ASTM D1744-92 (Withdrawn 2000) Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent.
- [20] ASTM D4809-09a (2009) Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method).
- [21] ASTM D664-07 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.
- [22] ASTM D976-06 Standard Test Method for Calculated Cetane Index of Distillate Fuels.
- [23] I. Tesseraux, "Risk factors of jet fuel combustion products," *Toxicol. Let.* **149**, 295 (2006).
- [24] Handbook of Aviation Fuel Properties, CRC Report No. 635, 3rd Edition, Coordinating Research Council (2004).
- [25] J. Gammon, "Aviation Fuel Quality Control Procedures," 4th Edition, ASTM Stock No.: MNL 5-4th, Baltimore, MD February (2009) http://www.astm.org/DIGITAL_LIBRARY/
- [26] S. Baena-Zambrana, S.L. Repetto, C.P. Lawson and J.K.-W. Lam, "Behaviour of water in jet fuel-A literature review," *Prog. Aeros. Sci.* **60**, 35 (2013).
- [27] A.B. Thompson and J. K.-W. Lam, "Water run-off in aircraft fuel tanks," *IMA J. Appl. Mathem.* **77**, 72 (2012).
- [28] J.K.-W. Lam, J.I. Hetherington and M.D. Carpenter, "Ice growth in aviation jet fuel," *Fuel* **113**, 402 (2013).
- [29] S.L. Repetto, J.F. Costello, B.De Lacy Costello, N.M. Ratcliffe and J.K.-W. Lam, "The Development of Novel Fuel Dehydrating Icing Inhibitors," *SAE Intern. J. Fuels & Lubric.* **6**, 553 (2013).
- [30] ASTM D93-13, Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester, ASTM International, DOI: 10.1520/D0093.