UDC 665.732

n-BUTANOL BASED EMULSIFIED DIESEL FUEL PRODUCTION

A.R. Abbasov

SOCAR Foster Wheeler Engineering LLC
6, Ali Valiyev str., AZ1060, Baku, Azerbaijan,
e-mail: Adil.Abbasov@client.woodplc.com,

Received 28.12.2019

Physico-chemical properties of diesel fuel with a content of 1-5% dehydrated (99.5%) and watered (93%) n-butanol were studied. To obtain homogeneous mixtures, a rotary-type mixer was used at temperatures of 0-25° C. It found that the stability of diesel fuel containing 3% mass. dehydrated n-butanol at a room temperature is 60 days. An increase in the content of n-butanol to 5% leads to a decrease in the stability of the prepared mixture up to 45 days. Stability of the diesel fuel mixture with 3% 93% n-butanol is 5 days at normal, and not more than 3 days at a temperature of 0 ° C. Adding to this mixture a 1% emulsifier obtained on the basis of propylene oxide esters with petroleum acids makes it possible to obtain homogeneous diesel fuel while preserving all its physicochemical properties. In addition, it was found that when this mixture is burned, the content of toxic gases, such as carbon oxides, nitrogen and sulfur, in the exhaust gas composition decreases by 24%, 16% and 12%, respectively as compared to the burning of butanol-free diesel fuel.
Keywords: *n-butanol, alternative fuel, emulsifier, exhaust gas*
DOI: 10.32737/2221-8688-2020-1-61-67

1. Introduction

Recent trends in environmental restrictions make it necessary to upgrade the use of alternative types of raw materials used for transportation purposes such as motor fuels, bio-based alcohols and other oxygen-containing components. All things considered, the use of environmentally friendly raw materials for producing automotive fuels such as diesel is the main objective of today's industry. As compared to other lighter fossil, the derived fuels for diesel engine produce more particulate matter-PM, more smoke, and nitrogen oxides-NOx with high thermal efficiency and lower carbon monoxide-CO and hydrocarbon-HC emissions. Specifically, the reduction of NOx and smoke emissions by Exhaust Gas Recirculation (EGR),variety of catalytic converters, high-pressure injection systems and as well as oxygenated fuels were investigated by any researchers. The major challenge associated with diesel engine is the use of alcohols in higher percentage mixed with diesel fuel. However, the limited capability of miscibility at a lower temperature and the minimum required modification in fuel delivery systems restrict the use of alcohols in the diesel fuel. A closer look at the statistics reveals that the automobile engines provide more than 80% of emissions to the atmosphere while a share of road transport in the emission of harmful substances reached up to 5 kton per day [1].

Ethers of fatty acids and alcohols are one of alternative ways of using oxygen-containing components where indicative parameters of engine fuels can be improved. Indeed, the presence of oxygen atoms in these types of additives provides a more complete combustion of the fuel, which makes the products combustion environmentally reliable and safer. Furthermore, the fuels above are nearly undepleted raw material base - both mineral (natural gas, coal, oil shale) and organic (potato, beet, vegetable oils and their waste, algae, etc.) giving an advantage of using the above as raw material [2-6]. Availability of n-butanol production facilities makes the use of alcohols as additives in diesel fuels economically feasible.

There are two main possible ways to use n-butanol;

1) in the form of an emulsion of mineral diesel fuel and watered alcohol (i.e., azeotropic mixture of n-butanol and water);

2) as a mixture for diesel fuel and absolute (anhydrous) alcohol.

In accordance with the experiments conducted above, the above-mentioned capabilities significantly reduce emissions resulting from combustion in a diesel engine, mainly due to the following main factors:

a) decrease in maximum combustion temperatures because of high heat of evaporation of n-butanol (592 kJ / kg for n-butanol against 230-250 kJ / kg for diesel fuel) which leads to lowering temperature, and consequently, to reduction in NO_x emissions;

b) presence of an oxygen atom in n-butanol molecules leads to reduction of harmful emissions in the exhaust gases that derived through internal combustion engines;

c) quality of fuel mixing process diminishing the toxicity values in the exhaust gases during the combustion of diesel fuels is due to the low boiling point of n-butanol (116-118°C in n-butanol versus 160-360°C in diesel fuel) which leads to rapid evaporation of n-butanol from mixture and additional turbulence to diesel fuel due to such evaporation rate [7, 8]. When it comes to stability factors in case of usage the absolute n-butanol, it is worth to note that in the preparation of mixed fuels it needs to be further upgraded which put under the question of mixtures stability guarantee at low temperatures. In that case considering the usage of available emulsifiers which ensuring the stability of alcohol-diesel mixtures the diesel fuel-n-butanol-emulsifier is recommendable and do not adversely affecting the other properties of the compounds obtained.

2. Experimental part

Experiment is carried out in order to identify properties of commercial diesel fuel with a content up to of 5% n-butanol with 93% and 99.5 % purity. Also, emulsifier (EM) is added to the mixture that is obtained on the basis on petroleum carboxylic acids and propylene oxide.

Properties of commercial diesel fuel and EM are given in Tables 1-2.

Table 1. Commercial diesel properties

Parameters	Values
Cetane number	50
Density at 20°C, кg/m^3	840
Fractional composition, °C	
IBP	180
10% distilled at	225
50% distilled at	275
90% distilled at	345
EBP	360
HC content, %:	
Aromatics	25
Parafins-naphthenes	70
Unsaturated	5
Kinematic viscosity at 20°C, mm^2/s	3.1
Acidity, mg KOH/100 sm^3 fuel	0,04
Iodine number, g I/100 g fuel	2,4

Temperature of, °C:	
Flash point	65
Pour point	-30
Cloud point	-28
Total sulphur content, ppmw	100
Test on a copper plate at 100°C for 3 h	Pass
Coking of 10% residue, % wt	0,021

Table 2. Synthesized emulsifier (EM) properties

Parameters	Values
Density at 20°C, кg/m^3	963
Acidity, mg KOH/100 g fuel	0
Iodine number, g I/100 g fuel	0
Kinematic viscosity at 20°C, mm^2/s	4.0

Ultrasonic generator UIP2000hd used for experiment on the preparation of diesel-n-butanol mixtures at room temperature. Mixer speed rate was 600 rpm, efficiency around 85%, operating frequency 1–20 kHz, operating amplitude was around 50 -100%, power consumption 200-240V, frequency of alternating current 48-63 Hz. In table 3 the outcomes of homogeneity of the mixtures were summarized.

Table 3. Homogeneity of diesel-n-butanol mixtures in time length depending on n-butanol content

	99.5% pure n-butanol in diesel fuel, % wt.		
	1%	3%	5%
Appearance of the mixture on the day of preparation	transparent	transparent	transparent
Stability of the mixture at a temperature of 25°C, day	80	60	45
Stability of the mixture at 0°C, day	60	45	25
	93.0% n-butanol content in diesel fuel, % wt.		
	1%	3%	5%
Appearance of the mixture on the day of preparation	Slightly coalescing liquid	Slightly coalescing liquid	Slightly coalescing liquid
Stability of the mixture at a temperature of 25°C, day	8	5	2
Stability of the mixture at 0°C, day	3	3	1

For different mixture content, for instance, diesel fuel with 1 % wt. anhydrous n-butanol preserves the transparency at a room temperature within 80 days. Of interest is that the n-butanol content in the diesel fuel reduces the stability period of the mixture to 60 and 45 days respectively. During diesel product handling process or storage where a temperature drops to 0°C, it then may lead to a decrease in the stability period of the compounds up to 60 days for a 1% n-butanol content and 25 days for 5% compounds, respectively. Thereafter, the mixture at first slightly grows turbid, and then the size of n-butanol droplets gradually increases, and the mixtures are stratified into diesel and alcohol layers. By using watered n-butanol with 93% purity it was observed that compounds obtained using an ultrasound sonotrode, slightly coalescing mixtures are formed, and the stability is not more than 8 days at room temperature and 1 day at 0°C temperature. To improve the resistance of mixture the 1% wt. emulsifier (EM) was added – this was synthesized on the basis of natural petroleum acids and propylene oxide. This compound retains stability for ≥80 days from the date of preparation.

The main properties of diesel fuel with a content of 3% wt. mass n-butanol and 1% wt. mass emulsifier are presented in Table 4.

Table 4. Commercial diesel fuel properties with the mixture of 3% wt. mass n-butanol and 1% wt. mass synthesized emulsifier

Parameters	Values
Cetane number	49
Density at 20°C, кg/m^3	841
Fractional composition, °C	
IBP	181
10% distilled at	224
50% distilled at	280
90% distilled at	335
EBP	355
HC content, %:	
Aromatics	24
Parafins-naphthenes	72
Unsaturated	4
Kinematic viscosity at 20°C, mm^2/s	3.2
Acidity, mg KOH/100 sm^3 fuel	0.03
Iodine number,g I/100 g fuel	2.4
Temperature, °C:	
Flash point	63
Pour point	-35
Cloud point	-31
Total sulphur content, ppmwt	100
Test on a copper plate at 100°C for 3 h	Pass
Water content, % wt	0.015
Coking of 10% residue, % wt	0.022

In Table 4 the mixture of commercial diesel fuel with the addition of 3% wt. mass n-butanol and 1% wt. synthetic emulsifier mixture properties is shown in line with requirements of the local AZS 3536601.243-2015 standard [9] for diesel fuels currently produced at the H. Aliyev oil refinery. By reviewing the properties such as density, kinematic viscosity, flash point and boiling point we can see that the values slightly swinged while properties remain within the limits of the local standard. Low-temperature characteristics of the obtained compound is improved whereas the pour point decreases by 5° C to make up - 35 ° C. Introduction of oxygen-containing compounds such as n-butanol and emulsifier into the composition of diesel fuel has also a significant beneficial effect on the exhaust gases composition generated during the combustion (Table 5).

Table 5. Exhaust gases composition before and after the introduction of n-butanol and emulsifier into the commercial diesel

Exhaust gases composition	Commercial diesel fuel emission level, wt %	Commercial diesel fuel +3% wt. n-Butanol+1%wt. Emulsifier, wt %	Decreased emission level, % (oxiginated/non oxiginated x 100%-100%)
CO	0.83	0.63	24
NO_x	0.61	0.51	16
SO_x	0.61	0.54	12
Smoke	20.4	14.2	31

CO emission is higher at lower loads for n-butanol-diesel fuel mixture. It is mainly explained as being due to the fact that n-butanol has latent heat of evaporation higher than that of diesel fuel. Owing to lower vaporization rate and lower cycle time, there is no chance for complete fuel combustion that results in considerable increase in CO emissions. At higher loads, there is enough time available for combustion to occur, better mixing and oxygen that results in complete combustion and lower CO emissions. According to experiments outcome described in Table-5, carbon monoxide release decreased by 24% for mixed fuel that consisted of 3% wt. n-Butanol+1%wt. Emulsifier, wt %.

With reference to the NOx rate of formation, it is a primary function of flame temperature, residence time, and oxygen content in the combustion chamber. High latent heat of vaporization of n-butanol results in reduced flame temperature and NOx emission accordingly in diesel –n-butanol blends compared to diesel fuel at low loads due to lower calorific value. Based on experiments outcome described in Table-5 nitrogen oxides release dropped by 16% for mixed fuel that consists of 3% wt. n-Butanol+1%wt. Emulsifier, wt %. But at higher loads due to greater fuel injection where the combustion temperature and oxygen availability are higher, the NOx has increased n-butanol percentage in the blend compared to neat diesel. Furthermore, for sulphur emission with the introduction of the composition of diesel fuel 3% wt. n-butanol and 1% wt. emulsifier can reduce the content in the exhaust gases of sulfur oxides by 12%.

It has to be kept in mind that the smoke effect with engine loads depends on different fuel-N-butanol blend percentage. Experience shows that smoke opacity is higher at low loads due to the short combustion cycle at high speed. Furthermore, long delay period, shortage of oxygen is observed due to improper mixing or high concentration of diesel fuel. But smoke opacity is higher for n-butanol blends as compared to diesel fuel. Diesel fuel has poor evaporation rate where n-butanol owns high latent heat of evaporation. On the other hand, high volatility of n-butanol has a serious effect on the reduction of smoke opacity, especially at high engine loads. Table-5 shows that the smokiness for mixed fuel which consisted of 3% wt. n-Butanol+1%wt. Emulsifier, wt % reduced by 31%.

Conclusion

As observed from the study, through the introduction of n-butanol and emulsifier into the commercial diesel fuel 2 major improvements are achieved:

1. Increasing the diesel fuel production due to non-oil feedstock resources. This experimental work demonstrated that the alcoholic fuels mixed with emulsifiers which are renewable energy sources are capable to replace diesel practically.

2. Improvement of low-temperature properties by diminishing harmful exhaust gas composition. SOx, HC, CO and smoke emissions reduced as alcohol concentration rose in diesel fuel. Finally, from the experimental study it can be observed that the n-butanol together with emulsifiers can be a good option for reducing fossil-derived fuel use in diesel engines to ensure heightened energy security of the country through decrease in fossil fuel market prices. Consequently, both achievements contribute to the economic feasibility and reduction of environmental emissions.

References

1. Tutak, W., Szwaja S., Lukacs K. Alcohol-Diesel Fuel Combustion in the Compression Ignition Engine. *Fuel,* 2015, vol.154, pp. 196-206. DOI: 10.1016/j.fuel.2015.03.071
2. Nayyar Ashish. Characterization of n-Butanol Diesel Blends on a Small Size Variable Compression Ratio Diesel Engine: Modeling and Experimental Investigation. *Energy Conversion and Management.* 2017, vol. 150, pp. 242-258.
3. Atmanlı, Alpaslan & Yilmaz, Nadir. A comparative analysis of n-butanol/diesel and 1-pentanol/diesel blends in a compression ignition engine. *Fuel*, 2018, vol. 234, pp. 161-169.
4. Swamy RL, Chandrashekar TK, Banapurmath NR and Khandal SV. Impact of Diesel-butanol Blends on Performance and Emission of Diesel Engine. *Oil Gas Res.* 2015, vol. 1, issue 1, p.1-7. DOI: 10.4172/2472-0518.1000101.
5. Lennox Siwale, Lukacs Kristof, Torok Adam, Akos Bereczky, Makame Mbarawa, Antal Penninger and Andrei Kolesnikov. n-Butanol-Diesel (D2) Blend Fired in a Turbo-Charged Compression Ignition Engine: Performance and Combustion Characteristics. In book: Improvement Trends for Internal Combustion Engines. 2018, chapter 3, pp. 37-47. http://dx.doi.org/10.5772/intechopen.72879
6. Hubert Kuszewski. Effect of Injection Pressure and Air–Fuel Ratio on the Self-Ignition Properties of n-butanol–Diesel Fuel Blends: Study Using a Constant-Volume Combustion Chamber. Energy & Fuels 2019, *vol. 33* (3), pp. 2335-2347. DOI: 10.1021/acs.energyfuels.8b04523.
7. Rakopoulos, Dimitrios & Rakopoulos, C. & Giakoumis, Evangelos & Dimaratos, Athanasios & Kyritsis, Dimitrios. (2010). Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. *Energy Conversion and Management - ENERG CONV MANAGE*. 2010 51. 1989-1997. 10.1016/j.enconman.2010.02.032.
8. Sendilvelan S. and Rajan K. Effect of butanol-diesel blends in a compression ignition engine to reduce emission. *Rasayan Journal of Chemistry (India),* 2017, vol. 10(1), pp. 190-194.
9. Local standard for diesel fuel AZS 3536601.243-2015

n-BUTANOL ƏSASLI EMULSİYALI DİZEL YANACAĞININ İSTEHSALI

A.R. Abbasov

SOCAR Azərbaycan Respublikası Dövlət Neft Şirkəti
AZ 1060, Bakı, Ə.Vəliyev küç., 6.
e-mail: Adil.Abbasov@client.woodplc.com

Məqalədə, tərkibində 1-5 %-dək susuzlaşdırılmış (99.5% li) və sulu (93% -li) n-butanol olan əmtəə dizel yanacağı qarışığının göstəriciləri təhlil edilmişdir. Homogen qarışıqların alınması üçün təcrübələr rotor tipli qarışdırıcıdan istifadə etməklə 0-25°C temperatur intervalında aparılmışdır. Müəyyən olunmuşdur ki, əmtəəlik dizel yanacağının tərkibində 3% kütlə dehidratlaşdırılmış n-butanol əlavə etdikdə, alınan qarışığın stabilliyi 60 gün davam edir. Lakin bu miqdarın 5% kütləyədək artması, qarışığın stabillliyini 45 günədək azalmasına gətirib çıxarır. 0°C temperatur şəraitində stabillik dövrü 1% susuzlaşdırılmış (99% təmizlikli) n-butanol qatıldıqda 60 gün, 5 % qatılıqda isə 25 gün-ə düşür. Dizel yanacağının 93%-li n-butanol ilə 3%-li qarışığının stabillik müddəti otaq temperatutunda 5 gün, 0 °C –də isə 3 gündən artıq olmur. Bu qarışığa 1% (kütlə) neft turşuları və propilenoksid əsasında alınan emulqator əlavə olunub. Nəticə olaraq təyin olunmuşdur ki, dizel yanacağının n-butanol ilə 3% - li qarışığına 1% kütlə emulqatorun əlavə edilməsi bütün normativ göstəriciləri saxlamaqla homogen dizel yanacağının alınmasına imkan verir. Eyni zamanda müəyyən olunmuşdur ki, tüstü qazlarının tərkibində karbon monoksid, azot və kükürd oksid birləşmələrinin miqdarının uyğun olaraq 24%, 16% və 12% azalması müşahidə olunmuşdur.
Açar sözlər: *n-butanol, alternativ yanacaq, emulsiya, tüstü qazları*

ПРОИЗВОДСТВО ЭМУЛЬСИОННОГО ДИЗЕЛЬНОГО ТОПЛИВА С ИСПОЛЬЗОВАНИЕМ Н-БУТАНОЛА

А.Р. Аббасов

Азербайджанская государственная нефтяная кoмрания SOCAR
AZ 1060, Баку, ул. А.Велиева 6,
e-mail: Adil.Abbasov@client.woodplc.com

Исследованы физико-химические свойства дизельного топлива при содержании в нем 1-5% обезвоженного (99.5 %) и обводненного (93%) н-бутанола. Для получения гомогенных смесей использована мешалка роторного типа при температурах 0-25 °С. Было установлено, что стабильность дизельного топлива с содержанием в нем 3% масс. обезвоженного н-бутанола при комнатной температуре составляет 60 дней. Увеличение же содержания н-бутанола до 5% приводит к снижению стабильности приготовленной смеси до 45 дней. Стабильность смеси дизельного топлива с 3%-ми 93%-ного н-бутанола составляет 5 дней при нормальной и не более 3 дней при температуре 0 °С. Добавление к этой смеси 1% эмульгатора, полученного на основе эфиров оксида пропилена с нефтяными кислотами, позволяет получить гомогенное дизельное топливо с сохранением всех его физико-химических свойств. Кроме того, установлено, что при сгорании этой смеси содержание токсичных газов, таких как оксиды углерода, азота и серы, в составе выхлопных газов уменьшается на 24%, 16% и 12% соответственно по сравнению с горением дизельного топлива без содержания бутанола
Ключевые слова: *н-бутанол, альтернативное топливо, эмульгатор, выхлопные газы*