BUTANOL USED AS A POTENTIAL ALTERNATIVE FUEL BLEND WITH N-DECANE AND DIESEL IN CI ENGINES FOR MARINE APPLICATION

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SUMMARY

For compression ignition engines, butanol is the most promising alternative fuel, in comparison with other alcoholic fuels. Butanol is superior to other alcoholic fuels because it has excellent physical and chemical properties that make it appropriate for diesel fuel blends. When butanol and diesel are blended, butanol is fully miscible in all proportions. Because butanol is hygroscopic, it does not absorb moisture from the environment. Because acetone-butanol-ethanol (ABE) fermentation may create butanol, it is commonly touted as a possible biofuel. This research is a significant step in gaining a thorough understanding of the effects of butanol on the fuel based on hydrocarbon. The fuel's molecular interactions mixes are studied using infrared (IR) spectroscopy. Binary mixes of butanol and n-decane, are investigated initially. After that, the mixture of butanol and diesel is investigated. When butanol is mixed with diesel, it forms strong bonds including the components of biodiesel that contain groups of esters. Furthermore, the possibility of employing Infrared spectroscopy for numerical mix analysis is assessed. The spectra are provided to enable a highly precise determination of the butanol concentration.

KEYWORDS

Fuel blends, Alternative fuels, Compositional analysis, Mixing effect

1. INTRODUCTION

Alcoholic chemicals are a type of alternative fuel that is widely used. Apart from its nature it has a low energy density and is particularly hygroscopic, ethanol is the most extensively diffused among them [1]. However, yeast-based fermentation techniques for producing ethanol from sugar feedstocks are extremely efficient. As a result, ethanol is a financially feasible biofuel. However, if higher alcohols could be produced without change in efficiency, then a higher energy density and lesser hygroscopicity. Butanol is a viable contender. It can be produced using a variety of renewable biomass sources, such as fermentation of acetone-butanol-ethanol (ABE) [2, 3]. Apart from agricultural materials, it may also be manufactured from monomer sugars like glucose [4], wood hydrolysate [5], whey permeates [6], and straw molasses [7] which offers a significant benefit because all of those resources are regularly discarded. It entails decreasing the rivalry between the production of biofuels and the production of food and animal feed [8]. When compared to ethanol, butanol has better chemical and physical qualities. The list of some of these characteristics is shown in Table 1.

Because butanol has a longer alkyl chain, it is more miscible in gasoline and diesel [12]. Apart from the existence of a polar OH group in which butanol is a fragment that is nearly non-polar. The lower vapor pressure, better energy density, and greater number of cetane are other advantages. Furthermore, it is less hygroscopic and corrosive, allowing it to be mixed into commercial fuels [13].

Table 1. Ethanol, butanol, and diesel fuel have different characteristics [9-11]

Characteristics	Ethanol	Butanol	Diesel
Density in g/cm^3	0.788	0.809	0.82-0.845
Specific energy, MJ/kg	26.8	33	42.5
Melting point, °C	–115	–89	
Boiling point, °C	78	118	170–390
Auto ignition temperature, °C	400	325	222
Flashpoint, °C	11	36	>55
Cetane number	8	26	>51
Octane number	130	96	

According to Zhang et al. discovered, adding butanol to heavy-duty diesel engines reduces pollutant emissions [14]. The surface tension and viscosity are also key characteristics for atomization and spray production inside the engine. Butanol has a viscosity that is around double that of ethanol which is quite near to commercial fuels (Diesel) value [15]. Butanol's surface tension is also closer to diesel's than ethanol's [16]. Before mixing butanol with a commercial fuel, two critical prerequisites must be met: the effects of blending must be considered, and measuring mechanisms for calculating butanol concentration should be taken into consideration. Blending effects are significant because blends can display very physicochemical and thermodynamic properties that are not optimal behavior, resulting in property and engine performance prediction challenges. De-mixing within the tank should also be prevented. The conclusive goal should be to have a thorough knowledge of the architectural-property correlations such that properties may be determined from simulations, eliminating the need for numerous property measurements. Individual component characteristics and molecular interactions in the mixture must be included in applicable computer models' underlying knowledge. These interactions constitute molecular mixing effects, and as a result, affect microscopic and macroscopic behavior. Dimethyl sulfoxide aqueous solutions are common solvents and anti-freeze, are noteworthy and striking illustrations of these blending phenomena. The freezing point of the eutectic combination is lower than the ideal mixture. The dynamics and interactions between the molecules in the mixture are to blame for the depression [17-19]. Analytical procedures, on the other hand, are critical for ensuring fuel purity and optimizing engine performance but raise the complexity of commercial fuels [20]. Combined a growing need for fuel-efficient combustion and pollutant emissions necessitates the development of new control methods to optimize the combustion process. An instant gasoline evaluation between a smart vehicle and a gas station gasoline pump geared up with analytical instruments are example of such notions. The term "on-board fuel analysis" refers to the process of analyzing fuel before it reaches the engine. Knowing the exact composition of fuel allows you to manage and optimize the engine's performance. The primary barrier to such technology is undoubtedly the related expenses; as a result, there is a need to build powerful, dependable, and low-cost analytics. Analytical principles that are appropriate range from traditional ways like modern spectroscopic methods from chromatography. Quality characteristics evaluation in the samples of diesel using nuclear magnetic resonance (NMR) spectroscopy [21]. A recent overview of the uses of vibrational spectroscopy for fuel analysis was published [22]. In the case of diesel fuel analysis, infrared (IR) spectroscopy was shown to be a very useful instrument. In essence, it may provide data on the mixing effects as well as on the chemical composition. Near-infrared spectroscopy has also shown promise [23, 24]. In this study, commercial diesel fuel and butanol mixes are examined using infrared spectroscopy. It expands on our prior research into ethanol-gasoline mixtures [25, 26].

2. EXPERIMENT

Above 99.5% purity Butanol was bought and diesel was purchased and used as received. Using a microbalance, butanol and diesel blends were generated gravimetrically. In stages of 10 weight percent, butanol/diesel mixtures were created across the mass fractions ranging from 0 to 100 percent butanol. Because of the commercial diesel chemical complexity, fractions of mass rather than mole fractions have to be adopted. Agilent Technologies Cary 630 Fourier Infrared Transform Spectrometer was utilized to collect Infrared spectra of the blends and pure compounds. An overall reflection module with ZnSe attenuation was installed on the instrument. The spectra were collected with a range between 650 per centimeter and 4000 per centimeter. A backdrop was gathered and the cleaned module before a spectrum was recorded.

3. RESULT AND DISCUSSIONS

3.1 INFRARED SPECTRA OF DIESEL, N-DECANE, AND N-BUTANOL

Fig. 1 shows the spectra of IR for diesel, n-butanol, and n-decane samples without mixing. Hydroxyl group stretching vibrations, abbreviated as OH cause a strong and wide band in the butanol spectrum between 3000 and 3600 cm^{-1}, which may be ascribed to the butanol spectrum. CH stretching modes may be discovered in the 2700–3000 cm^{-1} range. In all spectra, the fingerprint zone, defined as wave numbers less than 1500 cm^{-1}, is dominated by CC stretching modes and CH deformation. Within the regions of CH stretching and fingerprints, the diesel and decane spectra are extremely close. This indicates not only that n-decane is an excellent substitute from a spectroscopic standpoint, but also diesel includes a proportion of medium-chain hydrocarbons.

The appearance of extra peaks in the diesel spectrum at roughly 1750 and 1170 cm^{-1}, which are shown by arrows, is the primary difference between the two spectra. These peaks are caused by the ester groups' C-O and C=O stretching vibrations. Ester compounds are common in biodiesel. As a result, the IR spectrum indicates the presence of biodiesel in commercial diesel. According to the EN 590 standard, this proportion can be up to 7%.

3.2 DIESEL-BUTANOL BLENDS

Butanol/diesel mixes' infrared spectra were recorded and evaluated as the actual molecular composition of gasoline is uncertain, mixes were constructed in mass fraction terms only. The major ingredients of diesel, according to the spectrum, appear to be hydrocarbon and a small proportion of biodiesel. The spectra of a diesel-butanol mix shift

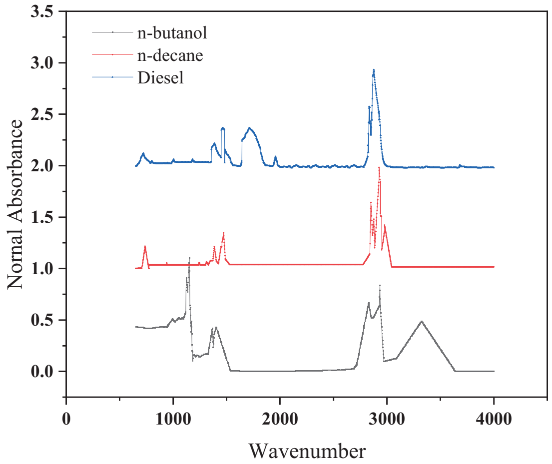

Figure 1. Normalized IR spectra of diesel, n-decane and n-butanol

in a predictable way as the composition changes. The sample of diesel includes polar ester groups with partially negatively charged oxygen atoms. As a result, hydrogen bonding or dipole-dipole interactions among the groups of ester and the groups of OH of butanol of mixed sample can be created.

3.2.1 Effects of Blending

The consequences of combining butanol and diesel may be examined from the diesel as well as butanol perspectives. The ester compounds' C=O groups are the most common locations for molecular interactions with butanol's OH groups. In the sample of diesel, the vibration peaks of the C = O stretching are at 1748 per centimeter. A second peak arises in the mixes' spectra at 1728 cm^{-1}.

The groups of C=O which are H-bonded to OH groups account for the second peak. The strong H bond causes the covalent C=O bond to weaken, resulting in the redshifted mode. Both peaks are identical in strength for low diesel concentrations, i.e. < 40%. This suggests that a considerable portion of the groups of ester are H-bonded with the molecules of butanol, but not all of them. This might be owing to the steric barrier, as well as the fact that butanol-butanol H bonds are more stable and so preferable. The C=O groups with H-bonded peaks grow only marginally when diesel mass fractions surpass 0.5, but the C=O groups without bounded maintain their trend of the peaks. Its rise gets higher until it reaches 0.7. The H-bonded C=O peak remains nearly constant in the same location. This backs up the theory that there are just a few types of ester groups that can interact with butanol.

The interactions of molecules of butanol can be investigated through an examination of the stretching band of OH. The change in the profile of the fitted Gaussian center wavenumber is a function of composition. The result shows a consistent blue shift with a nearly linear trend. Variation in the mathematical connection of the trend butanol/diesel instance should not be misinterpreted, since it might be due to graphing molar and mass fractions. The most important observation is the blue shift. In the C=O groups, the establishment of an H bond frequently results in the stretching mode in redshift. However, when it comes to butanol, it's important to remember that the plain liquid already has a lot of hydrogen bonds. As a result, the blue shift is observed to the original strong connection. This implies that H bonds between hydroxyl groups and C=O are weak, bolstering our theory of better energy stability above.

3.2.2 Quantitative Analysis

The feasibility of measuring butanol content in diesel blends quantitatively was examined. The IR spectra may be used to quantify butanol concentrations in addition to obtaining information on molecular mixing events. Two technique-based tests have been implemented for this aim. The first is a simple approach by the Beer-Lambert equation as shown in Fig. 2, according to this equation, the absorbance is proportional to the absorbing species' concentration at a given wavelength.

A simple approach, originally designed to detect the concentration of dissolved complex compounds in liquids of ionic, was used for a structured evaluation of the spectrum locations, where the BL equation can be used to accurately measure the concentration of butanol [27-29]. For every spectral data point, the absorbance values are a function of concentration and are fitted using a function of linear equation. The coefficient of determination and slope of the function are calculated using this fit. A higher absolute value of the slope and a higher coefficient of determination are both desired for quantitative measurements. A sharp slope denotes a greater sensitivity to concentration fluctuations, and an R^2 close to 1 suggests that the absorbance and concentration values are well correlated. The chemometrics toolbox contains less effortless but well-established ways

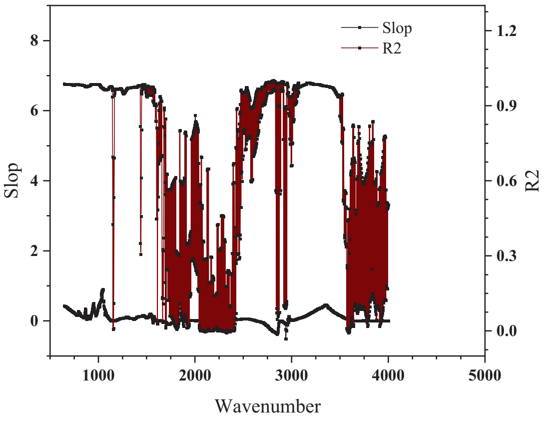

Figure 2. Spectra of the normalized slope of diesel/ butanol blends

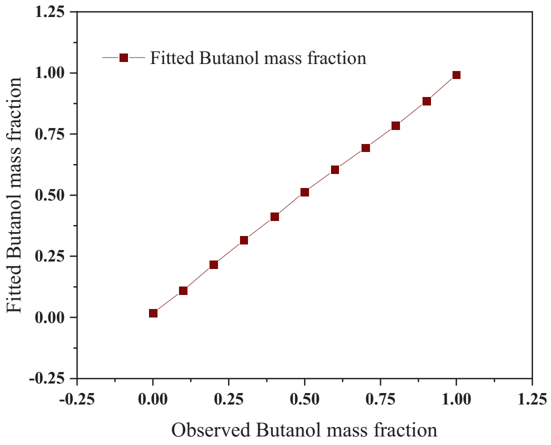

Figure 3. PLSR analysis of butanol/diesel blends

of measuring vibrational spectra [30, 31]. Chemometrics is a set of mathematical procedures for identifying spectral characteristics that are related to the parameter of interest. Parameters include the age of a whiskey [32], the temperature [33], and the concentration [34, 35] of a class of chemicals [36-38]. When absorbency likewise rises with butanol saturation, the OH stretching area returns to a steeper value. Compounds containing hydroxyl groups are not present in the fuel. The CH stretching area has primarily negative slopes, suggesting that the hydrocarbon is the dominant component. The contributions from butanol dominate the fingerprint area. Again, the best spectral area to make quantitative measurements appears to be in the range from 1000 to 1100 per centimeter, where the highest values of slope and R^2 values may be obtained. The values of absorbance obtained at 1035 per centimeter coupled with the fitted function as a function of butanol mass percent, as an example. The spectrum of R^2 has a local maximum of 0.982 at this spectral location.

The partial least-squares regression approach was implemented to examine the Infrared spectrum of butanol mixtures in the investigation. The correlation between the mass fraction's determined gravimetric butanol concentration, the PLSR is used to calculate the corresponding values, and only normal deviations are shown from the straight line. As a result, shown in Fig. 3, it may be stated that PLSR can ascertain the butanol concentration in its diesel mixes.

3.3 BUTANOL/N-DECANE BLENDS

The butanol/n-decane spectroscopy merges with the spectra of the two pure molecules. The spectra vary extremely consistently with composition, as can be seen. This is to be expected, given that decane is a pure hydrocarbon with little ability to form significant hydrogen bonding or polar interactions. The only interactions of this sort in the mixtures will be between the butanol molecules hydroxyl groups.

3.3.1 Blending Effects

OH, stretching band may be used to explore the result of combining the polar and H bond interactions among butanol molecules, butanol, and decane. For this, a single Gaussian profile was fitted to each band in the spectrum of each unique blend. This fit may be used to estimate the band's core wavenumber with remarkable precision and reproducibility. The OH stretching band in pure butanol is located at 3326 per centimeter. The band steadily shifts in the direction of a greater wavenumber as decane concentration rises. The solid line, which displays an empirical function with the decane mole fraction as the variable x, emphasizes the shift's tendency. Decane is diluted and added to butanol causing a noticeable shift, and as the decane concentration rises, the slope becomes less steep. We employ the same mathematical formula since the behavior is qualitatively comparable to absorption transition saturation in fluorescence spectroscopy [39]. Due to the poor signal-to-noise ratio, the Gaussian fit's error bars grow fairly big for low butanol levels. However, because several data points in fit and a growing number of spectra were employed to establish suitable statistics, the resultant center wavenumbers remain on the trend curve. A blue change like this implies a strengthening of the OH bond, which means the hydrogen bonding is decreasing [40]. In other words, the H bonding network among butanol molecules becomes less stable as there is more decane in the mixture. Surprisingly, the blue shift is greater than that seen in prior research on ethanol-to-gasoline mixes [26]. This discrepancy can be attributed to butanol's larger alkyl chain length, which allows for stronger van der Waals interactions with decane molecules. The wide OH band's general shape and breadth, however, remain unchanged. This shows that even at high decane concentrations, butanol-butanol hydrogen bonding is still present, and a similar pattern is observed in the gasoline/ethanol system, leading to the conclusion that tiny clusters of ethanol develop [26].

3.3.2 Quantitative Evaluation

Infrared spectra offer numerical measures of butanol concentration in addition to obtaining information on molecular mixing events. Two techniques have been carried out for this aim. The initial is a simple approach focused on the equation of Beer-Lambert, which results in the absorbent at a given wavelength being directly proportional to the absorbing species' concentration. A simple approach, originally designed to detect the concentration of dissolved complex compounds in ionic liquids, was used for a structured evaluation of the spectrum locations, in which the Beer-Lambert equation may be applied to obtain an exact determination of butanol concentration [27-29]. The absorbance values for every spectral data point are shown as a concentration function, followed by a linear function used to fit the data. R^2 is the function's slope and coefficient of determination, which

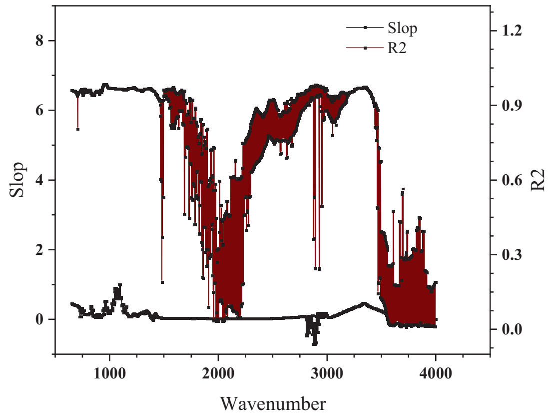

Figure 4. Spectra of the normalized slope of decane/ butanol blends.

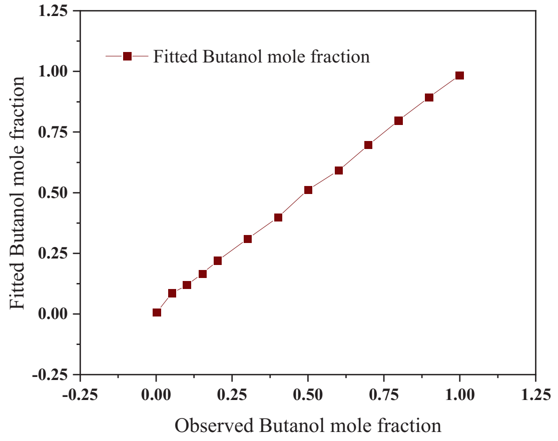

Figure 5. PLSR analysis of butanol/decane blends.

are calculated using this fit. The slope's great absolute value and a high coefficient of determination are both desired for quantitative measurements. A sheer slope implies a strong sensitivity to concentration changes and an R^2 close to one indicates that the values of absorbance and concentration are well connected. Fig. 4 shows the R^2 spectra and normalized slope.

There are various places in the normalized slope and R^2 spectra that appear to be acceptable for quantitative measurements. The concentration of butanol causes an increase in absorbance., resulting in a positive slope in the OH stretching zone. The CH stretching area has primarily negative slopes, suggesting that the hydrocarbon is the dominant component. Butanol contributions dominate the fingerprint region once again. The best spectral area for quantitative measures appears to be between 1000 and 1100 cm^{-1}, where the highest R^2 values and maximum slope values may be obtained. The absorbance value was obtained at 1078 cm^{-1}. The chemometrics toolbox contains prevalent methods for measuring vibrational spectra. Chemometrics is a set of mathematical procedures for identifying spectral characteristics that are related to the parameter of interest. The infrared blends' decane or butanol spectrum in this work were analyzed using partial least-squares regression, which is a widely used approach. PLSR determined the relation between the gravimetrically specified butanol concentration and the associated values. Fig. 5 shows only slight variations from the ideal straight line may be seen in the data points.

As a result, it can be stated that the PLSR approach is a good way to figure out how much butanol is in decane mixtures. Mixtures with other hydrocarbons should yield similar results.

4. CONCLUSIONS

From a spectroscopic standpoint, the possibility of using butanol as a biofuel in conjunction with traditional petrochemical fuels has been examined. Butanol and commercial diesel mixes were subjected to IR spectroscopy. The spectra enabled a molecular-level investigation of mixing effects as well as a quantitative analysis of butanol content. While blending effects are fascinating on their own, quantitative measurement will become a more relevant technique for observing the composition of fuel. The spectra of the decane or butanol mixtures revealed that the presence of isooctane reduces the hydrogen-bonded connections between butanol atoms. The hydrogen bonding network forms small clusters due to the molecules of butanol. On the other hand, their butyl chains enable non-polar hydrocarbon miscibility over the whole spectrum of combination fractions. A minor quantity of biodiesel was present in commercial diesel, as evidenced by spectral fingerprints of ester groups. Butanol hydroxyl groups can receive hydrogen bonds from these ester groups. An extra red-shifted C=O stretching mode results from such an H bond. Butanol molecule's hydrogen bonds, on the other hand, were shown to be more energetically stable.

Finally, it was discovered that IR spectroscopy is a reliable and accurate method for determining the quantity of butanol in diesel and decane. Both methods are efficient in producing quantitative results with a high degree of accuracy and sensitivity.

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