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Effects of Bioglycerol Based Fuel Additives on Diesel Fuel Property, Engine Performance and Emission Quality: A Review

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Abstract

Diesel engine emission is a major contributor of harmful pollutants viz., nitrogen oxide, hydrocarbon, carbon monoxide, carbon dioxide and smoke emission. To suit stringent emission norms, the polluting components in the fuels need substantial reduction. Blending of bioglycerol based fuel additives in diesel could satisfactorily meet emission norms. Notably, bioglycerol, one of the by-products of biorefineries proved as a prospective resource for sustainable production of valuable bioadditives to mitigate engine emissions coupled with enhancement of fuel properties. This article presents a comprehensive overview on various glycerol derived fuel additives and the reaction conditions involved in the production processes.

Keywords: engine emission, diesel, glycerol, additive, blends.

1. Introduction

Diesel engines are one of those among the transport related energy use which are popular due to its promising heavy-duty condition compatibility. However, diesel-fuelled engines possess major pitfalls viz., production of NOx, CO, particulate matter and HC which leads to emission restriction issues. In order to reduce the emanations of these harmful gases, several emission reduction systems are used. However, these systems are cost-intensive and cannot be used on long term basis. Thus, production of such harmful gases can only be mitigated through improvement in the combustion process by adding cleaner fuels (biofuels) or fuel additives (FA) [1]. Previously, FAME (Fatty Acid Methyl Ester) was used

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as FA with diesel; but, it leads to certain confinements. Thus, several studies have been performed to increase the diesel fuel qualities via application of FA [2]. FA from low value glycerol (Gly), a biodiesel by-product has proved to be a promising additive which can upsurge engine performance. However, production of these valuable additives requires adverse reaction conditions, making the process economically unattractive. Thus, it is of utmost importance to critically assess the process parameters that can favorably yield the desired additive through economically sustainable pathways. Effort has also been made to understand the effect of application of the FA on engine emission and performance.

2. Diesel Fuel Properties

2.1 Cetane Boosters

The cetane number of a fuel plays an important role in compression ignition (CI) engine. Therefore, fuel having low cetane number (CN) will exhibit long ignition delay, abnormal combustion, etc. Thus, many diesel fuel compositions comprise of ignition improvers to improve fuel quality. Triacetin (oxygen content 53.3%), a Gly derived ester serve as an effective replacement when blended with diesel or biodiesel [3]. Table 1 depicts the recent trends in triacetin (TAG) production using various heterogeneous catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Condition</th>
<th>(TAG) Selectivity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heteropoly acid; Bronsted Acid</td>
<td>AA: Gly 12:1; 60°C; 12h</td>
<td>20%</td>
<td>[4]</td>
</tr>
<tr>
<td>Niobiosilicate and mesoporous silicate of SBA-15</td>
<td>AA: Gly 9:1; 150°C; 4h</td>
<td>39 %</td>
<td>[5]</td>
</tr>
<tr>
<td>Silver exchanged phosphotunstic acid</td>
<td>AA: Gly 10:1;120°C; 15mins</td>
<td>5.2 %</td>
<td>[21]</td>
</tr>
<tr>
<td>12-tungstophosphoric anchored on MCM-41 and zirconia</td>
<td>AA: Gly 6:1:100°C; 6h</td>
<td>15%</td>
<td>[22]</td>
</tr>
</tbody>
</table>

#AA: Acetic acid

It has been well observed that only higher reaction time and temperature favors triacetin selectivity; thus, rendering higher operational cost.

Methylation of glycerol with dimethyl sulphate leads to the production of another value added chemical viz., glycerol dimethoxy ethers (GDMEs), and trimethoxy ether (GTME), a new oxygenate additive possessing comparable CN like TAG [6]. Mixture of 20 wt. % GDME and 80 wt. % GTME as diesel oxygenate, improves cetane number up to 58; thus, rendering less amount of unburnt engine exhausts. However, the reaction time for preparation is quite high making the process uneconomical. Table 2 represents other glycerol derived additives that are expected to enhance the combustion characteristics of the fuel.

2.2 Cold Flow Improver

Frusteri et al. [12] applied novel spherical silica supported Hyflon catalysts (SSHC) which, although showed high (97.4%) selectivity towards DTBG and TTBG with low selectivity towards monoethers; nevertheless, consumed extensive reaction time of 6h. However, usage of IB (isobutylene) for etherification, gets limited owing to hindered mass transfer resistance due to its immiscibility in Gly coupled with its higher cost. [13] Thus, TBG was considered as a secondary route for DTBG and TTBG production. To improve TBG synthesis, Viswanadham and Saxena [14] modified the reactor configuration into fixed bed reactor and achieved far better selectivity compared to batch reactor. Additionally, higher acetyl glycerol viz., diacetate (DAG) and triacetate (TAG) can also serve as a cold
flow improver. Figure 1 particularizes the effect of TAG addition to biodiesel on cloud point and pour point [15].

![Fig. 1. Effect of Triacetin on Biodiesel Quality [8].](image)

**2.3 Lubricity Improver**

Desulfurization required for diesel to meet environmental norms, eventually causes wear in fuel injection equipment. A lubricant lower friction losses and thus, increases fuel economy while reducing exhaust emissions. Knothe & Steidley [16] disclosed that the existence of mono-and diacylglycerols in the range of 100-200 ppm can provide sufficient anti-wear capacity; thus, ensuring normal operation of the motor injection system. Furthermore, glycerol monooleate also proved to be an effective diesel additive improving lubricity when blended with diesel [17]. Lapuerta et al., 2015 [11] reported the use of glycerol with used waste cooking oil (UCO) and animal fats (FA) to form a novel ester, FAGE, which when blended with diesel (Fig. 2) has been found to improve the lubricity property of the fuel.

Table 2. Glycerol Based Additives as Fuel Oxygenates

<table>
<thead>
<tr>
<th>Diesel fuel constitutes of n-</th>
<th>Type of Reaction</th>
<th>Yield/Selectivity (%)</th>
<th>Time (h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl glycerols</td>
<td>Etherification of Glycerol and Ethanol</td>
<td>70</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Diglycerol and Triglycerol Solketal</td>
<td>Condensation of Glycerol</td>
<td>33%</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>SOKETAL</td>
<td>Ketalization of Glycerol with acetone</td>
<td>94</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>1,3-dioxolane + 1,3-dioxane</td>
<td>Acetalization of Glycerol with</td>
<td>80/20</td>
<td>6</td>
<td>10</td>
</tr>
</tbody>
</table>

![Fig. 2. Wear Scar indicating Lubricity for FAGE/ diesel blend. [11]](image)
Exhaust Gas Emission Reducer

Smoke Emission Reducer

Smoke emissions, which occur due to improper fuel ignition, result in major air pollution. It has been established that usage of oxygenated compounds having higher CN produces cleaner burning of diesel fuels. Amongst the Gly based FA, a transesterified product of butan-2-one glycerol and methyl hexanoate leads to the production of Gly ketal ester which has been applied as a promising diesel FA [18]. It has been observed from Fig. 3a that E2 additive rendered reduced smoke density compared to other additives mentioned in this article. Table 3 extracted from the literature [18] depicts the effect of additive on diesel fuel properties.

<table>
<thead>
<tr>
<th>Blends</th>
<th>Density (kg/m³)</th>
<th>Viscosity (mm²/s)</th>
<th>Flash Point (°C)</th>
<th>Pour Point (°C)</th>
<th>Cetane Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>844</td>
<td>2.70</td>
<td>61.1</td>
<td>-10</td>
<td>45.60</td>
</tr>
<tr>
<td>K1 [1 wt. % of (2-ethyl-2-methyl-1,3-dioxolan-4-yl) methanol]</td>
<td>843</td>
<td>2.65</td>
<td>54.4</td>
<td>-13</td>
<td>46.28</td>
</tr>
<tr>
<td>K2 [2 wt. % of (2-ethyl-2-methyl-1,3-dioxolan-4-yl) methanol]</td>
<td>848</td>
<td>2.66</td>
<td>56.4</td>
<td>-15</td>
<td>46.05</td>
</tr>
<tr>
<td>E1 [1 wt. % (2-ethyl-2-methyl-1,3-dioxolan-4-yl) methyl hexanoate]</td>
<td>848</td>
<td>2.68</td>
<td>64.4</td>
<td>-16</td>
<td>49.41</td>
</tr>
<tr>
<td>E2 [2 wt. % (2-ethyl-2-methyl-1,3-dioxolan-4-yl) methyl hexanoate]</td>
<td>850</td>
<td>2.69</td>
<td>67.4</td>
<td>-18</td>
<td>48.30</td>
</tr>
</tbody>
</table>

3. NOx Mitigator

Emission of nitrogen oxides typically depends on engine performance. Presence of oxygenates in the fuel for reduction of particulates greatly heightens NOx emission. Fernando et al. [19] recognized thermal NOx as a major contributor. DAG and TAG were found to decrease NOx emission mitigating air pollution [6]. Also, ethers derived from Gly help in NOx reduction; since the hydroxyl groups present in it incorporates small amount of water molecules in fuels. A study carried (Fig. 3b) by Oprescu et al. [18] showed that NOx emission by glycerol ketal blended diesel was more compared to glycerol ketal ester blended diesel which can be attributed to the fact that presence of alkyl chain increases ignition delay periods of injected molecules.
Furthermore, etherified product of glycerol (GEM) being a promising fuel oxygenate [7] not only improves fuel properties but, also reveals no significant variations in NOx emission as revealed in Fig. 4.

3.3 HC and CO emission inhibitor
Several factors are accountable for CO emissions including, engine speed, air-fuel ratio, fuel type, injection timing and pressure. It has been proven that blended fuels result in lower CO and HC emission compared to neat fuel [20]. Oprescu et al. [18] blended glycerol ketals and glycerol ketal esters with diesel to assess the HC and CO emission characteristics. It can be observed from Fig. 5 that diesel blended with E1 additive rendered lowest HC emission whereas, diesel blended with E2 additive resulted lowest CO emission at higher engine speed.

4. Conclusion
It can be well apprehended from this review that glycerol based additives can effectively improve fuel properties via reduction of harmful exhaust emissions when blended with diesel or biodiesel. Thus, many research efforts are being undertaken to synthesize promising additives; nevertheless, high reaction time and temperature along with other severe operating parameters pose real challenge to the researchers and practicing technologists. Future efforts should, thus, be directed towards development of economically favorable reaction conditions and reactor systems that can render cost optimization for inexpensive production of such valuable additives.
References


