Possibilities for the utilization of waste glycerine as a fuel

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Abstract:
A significant increase in the production of fluid biofuels derived from vegetable oils has been observed in recent years. This is largely due to the depletion of crude oil resources with the consequent increase in the prices of petroleum fuels.

Methyl esters of higher fatty acids, commonly called Biodiesel, are made in the transesterification process involving the methanolysis of rape seed oil. Aside from the main product, also a glycerine fraction is produced. Biodiesel enjoys increasing popularity; however, the dynamic growth of its production results in the generation of large amounts of the glycerine fraction, which constitutes a major obstacle to the profitability of the process. The most common method of utilizing the glycerine waste has been so far to purify it to pharmaceutical glycerine, which finds application, e.g. in the pharmaceutical, food, or cosmetics industries. However, the high costs of glycerine waste purification and market saturation with glycerine urge that new, cheaper solutions be sought. An alternative can be the use of the glycerine fraction as a heat-generation fuel. Glycerine has a high calorific value, and can therefore be combusted in boilers as an addition to fuels. However, the chemical composition and physicochemical properties of these wastes deviate significantly from those required of fuel oils.

The paper deals with the possibility of using the glycerine fraction as a heat-generation fuel. It provides results of laboratory analyses concerning the physicochemical properties of pharmaceutical glycerine, the glycerine fraction, and the glycerine-fuel oil mixture with a different mass share of the glycerine fraction. The above-mentioned fuels were combusted in an open space and in a warmed-up ceramic chamber. The effect of their viscosity on burner performance was tested. The effect of the glycerine fraction share on combustion gas composition, including NO\textsubscript{x} contents, was also examined.

1. Introduction

In the era of searching for solutions to improve the quality of natural environment, an important role is played by investigations into the use of unconventional, renewable sources of energy. This is largely connected with the depletion of petroleum and natural gas resources, which, as a consequence, leads to an increase in energy prices. The above problems could be prevented by introducing fuels produced in the waste recovery process, that is alternative fuels, into the market. Early studies on this type of fuels were conducted in the eighties of the last century, and a considerable increase in their production and fuel market share has been observed ever since. For the ecologic and economic points of view, introducing alternative fuels brings about a number of advantages, e.g. a lower operation cost, reduced emissions of toxic compounds, and above all, the energy independence of a country or region thanks to the production from its own mineable raw materials and agricultural products [1,2].

Among the major alternative energy sources are undoubtedly fuels obtained by processing the products of living organisms, so called biofuels. Obtained from, e.g., rape seeds methyl esters of higher fatty acids, commonly called biodiesel, are, at the present stage of technology, definitely the most important fuel to supplement traditional diesel oils. Biodiesel can be used
as a fuel for the majority of diesel engines. Unlike diesel oil, the biofuel is biodegradable, and the emissions of harmful chemical substances during its combustion is lower. A basic drawback in the production of biodiesel is the formation of a by-product, which is the glycerine fraction [2,3]. The dynamic growth of biodiesel production results in the generation of large quantities of the glycerine waste, which presents a major obstacle to the profitability of the process.

So far, the most common method of utilizing the glycerine fraction has been its purification. Pure (pharmaceutical) glycerine finds a wide application, e.g. in the pharmaceutical, food, cosmetic and leather industries, as well as for the production of explosives, dyestuffs, brake fluids and refrigerants. However, the high costs of waste glycerine purification and saturating the market with pharmaceutical glycerine encourage searches for new, cheaper solutions. An alternative can be the utilization of the glycerine fraction as a fuel. Glycerine has a high calorific value (approx. 30 MJ/kg), and therefore can be combusted in boilers as an addition to fuels. However, the chemical composition and physicochemical properties of this type of waste deviate significantly from those required of fuel oils [3,4]. The solution could be to mix waste glycerine with fuel oil so as to obtain a mixture that will meet the standards for heat-generation fuel.

**Production of higher fatty acid methyl esters**

Methyl esters of higher fatty acids are produced in the transesterification process involving the methanolysis of glycerine oil to higher fatty acids in the presence of either a basic or acid catalyst. As the basic catalyst, sodium hydroxide is chiefly used; the acid catalyst is most often sulphuric acid. The raw material is rape seed oil; soya bean oil, sunflower oil, or animal fats are less often used. The production process consists in slow adding of heated oil to the mixture of alcohol and the catalyst. The reaction of synthesis of higher fatty acid methyl esters proceeds as follows:

\[
\text{higher fatty acid ester} + \text{glycerine oil} + \text{methyl alcohol} \xrightarrow{\text{catalyst}} \text{higher fatty acid methyl ester} + \text{glycerine}
\]

As a result of the reaction, two phases form: the ester phase and the glycerine phase. The ester phase are methyl esters that collect at the top of the process tank due to their lower weight compared to the glycerine phase. Whereas, the heavier glycerol, as a by-product, sinks to the bottom [5,6].

**Methods of waste glycerine utilization**

The glycerine fraction, as a by-product, form always in the amount above 12% in relation to the esters obtained. This is so called waste glycerine (glycerine fraction, crude technical glycerine), which, apart from glycerine itself, contains also soaps, methanol, water, non-completely esterificated vegetable oil, the catalyst, proteins, phospholipids, and other contaminants. The chemical composition of the glycerine fraction is diverse, depending on the quality of the raw material used for production of esters, but also on the technology of the methanolysis process. The most common method of utilization of waste glycerine has been so far its purification to obtain pharmaceutical glycerine. However, the amounts of the waste generated during the production of biofuels exceed considerably the needs of the pharmaceutical and the cosmetic industries [5,7,8]. Therefore, other solutions to the problem of its utilization are being sought for. Attempts to use the glycerine fraction for the purposes
of heat engineering were undertaken e.g. in the United States, but also in Poland this subject matter was addressed [4,9,10].

The present paper reports the results of tests of combustion of the glycerine fraction. Glycerine was combusted in the open in a heated ceramic chamber, where combustion gas composition was controlled using a catalyst. The effect of the percentage content of the glycerine fraction in the light fuel oil – glycerin e fraction mixture on the emission of nitrogen oxides, as well as on burner performance [11,12,13].

2. Materials and the test stand

Glycerine was obtained from the Polish Refinery of Trzebinia. The chemical formula of technical glycerine: C$_3$H$_8$O$_3$; the composition: glycerine, 80% min.; ash, 5% min.; organic compounds aside from glycerol, 6% max.; water, the balance.

Technical glycerine (Fig. 1a) is a brown, oily liquid with a specific, sharp smell. Pharmaceutical glycerine (Fig. 1b) is colourless and odourless and has a thicker consistency compared to technical glycerine.

![Fig. 1. View of technical glycerine (a) and pharmaceutical glycerine (b)](image)

Tests of co-combustion of glycerine with fuel oil were carried out. For this purpose, light fuel oil–glycerine mixes with a glycerine percentage share of 20%, 40%, 50%, 60%, 80% and 90%, respectively, were prepared. The mixes were combusted using a Giersch burner. The burner was installed in a ceramic chamber (Fig. 2) preheated to a temperature of 1000°C.

![Fig. 2. Schematic of the experimental setup with a ceramic chamber]((image))
3. Testing results and discussion

Technical glycerine and pharmaceutical glycerine were combusted in the open in ceramic vessels [11,12]. The glycerine was brought to its boiling point with a gas burner.

Both technical glycerine and pharmaceutical glycerine combust in the open (Fig. 3). Pharmaceutical burns out almost completely (99.7%), whereas technical glycerine leaves approx. 30% of residues after burning (Fig. 4).

Tests of combustion and co-combustion of glycerine were carried out [13]. Fuel oil, a glycerine fraction, pharmaceutical glycerine, a mixture of both glycerines in the proportion of 1:1, and a glycerine fraction-light fuel oil mixture in a glycerine percentage share of 10%, 20%, 40%, 50%, 60%, 80% and 90%, respectively, was introduced perpendicularly into a ceramic chamber heated up to a temperature of 100°C through a sprayer constructed based on the Giersch burner.

The contents of carbon dioxide, carbon monoxide, nitrogen oxides and oxygen in the combustion gas were determined using an analyzer. The value of the excess air factor was also determined. The test results are given in Table 1.
Table 1. Results of the tests of combustion of diesel oil, technical glycerine, a mixture of both glycerines, as well as a mixture of fuel oil and technical glycerine [11]

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Fuel oil</th>
<th>Technical glycerine</th>
<th>Pharm. glycerine</th>
<th>Oil + technical glycerine (1:1)</th>
<th>Techn. glycerine + pharm. glycerine (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂, %</td>
<td>8.4</td>
<td>8.1</td>
<td>7.6</td>
<td>8.5</td>
<td>8.6</td>
</tr>
<tr>
<td>O₂, %</td>
<td>5.6</td>
<td>6.8</td>
<td>7.5</td>
<td>6.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Λ</td>
<td>1.37</td>
<td>1.48</td>
<td>1.36</td>
<td>1.39</td>
<td>1.39</td>
</tr>
<tr>
<td>NO, ppm</td>
<td>51</td>
<td>42</td>
<td>49</td>
<td>42</td>
<td>54</td>
</tr>
<tr>
<td>NO₂, ppm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NOₓ, ppm</td>
<td>51</td>
<td>42</td>
<td>50</td>
<td>42</td>
<td>54</td>
</tr>
<tr>
<td>T °C</td>
<td>601</td>
<td>618</td>
<td>621</td>
<td>612</td>
<td>651</td>
</tr>
<tr>
<td>CO, ppm</td>
<td>480</td>
<td>615</td>
<td>0</td>
<td>283</td>
<td>0</td>
</tr>
</tbody>
</table>

The results of the tests indicate lower emissions of CO and NOₓ during the combustion of the mixture of technical glycerine and fuel oil (1:1) compared to the sole oil (Table 1). Trials on co-combustion of pharmaceutical glycerine with oil were undertaken, but the mixture formed was too thick to be able to be sprayed and burned in the chamber.

The effect of the percentage share of the glycerine fraction in the light fuel oil–glycerine fraction was examined for the contents of NOₓ in the combustion gas [13]. The results are represented in the diagram below (Fig. 5).

![Fig. 5. Effect of the glycerine fraction addition on the contents of NOx in the combustion gas](image)

In the case of the 10% glycerine share, the value of NOₓ was 41 ppm, whereas for the 90% glycerine share, this value was 45 ppm. It can therefore be inferred that the share of glycerine in its mixture with fuel oil has no significant effect on burner performance.

The effect of the glycerine fraction content of the mixture on burner performance was also examined (Fig. 6).
With increasing glycerine share in the mixture, the performance of the burner decreases. As follows from the diagram, for the combustion of oil with the 10% share of glycerine, the burner performance is two times higher compared to the combustion of the sole glycerine. This can be caused by the much higher viscosity of the glycerine fraction. This is also associated with the difficulties in spraying it in the chamber.

4. Summary

The preliminary results presented in this paper encourage further investigations to be conducted concerning the use of waste glycerine as mixed with a liquid fuel. It is planned to determine the physicochemical properties and chemical composition of the mixture of waste glycerine with fuel oil, to develop an appropriate technology for its preparation, and, above all, to carry out a detailed analysis of the emissions of combustion compounds using a gas chromatograph coupled with a mass spectrograph.

Accomplishing the above goals, as well as finding appropriate burner installations to ensure the proper combustion of the glycerine fraction offer a great hope for the dissemination of using it as a heat-generation fuel.

5. References

[12] A. Bala; „Wykorzystanie gliceryny odpadowej jako paliwa ciepłowniczego”; Projekt na konkurs EKO 2009 w dziedzinie ochrony środowiska; niepublikowany w materiałach naukowych.