

Determination of the heat of combustion for pure and mixed fuels

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Summary: Combustion plays a crucial role in many industrial processes, such as heating and power generation. Determining the heat of combustion values for different fuels is an essential step towards improving combustion processes by improving combustion efficiency or reducing emissions. In this study, a Junkers flow calorimeter was used to determine the heat of combustion for both the pure and mixed fuels. Although the methodology used in our study is not unique, our results provide insights into the heat of combustion values of four different fuels: corn bio-ethanol, isopropanol, Bioseptol 80, denatured alcohol, and their mixtures. Overall, our study offers insights into the heat of combustion values for different fuels, provides a standardized approach for measuring the heat of combustion that can be used to replicate the results and points out the main factors that influence their accuracy.

Key words: heat of combustion, fuel, fuel mix, calorimetry, combustion

Wyznaczanie ciepła spalania dla paliw czystych i zmieszanych

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Streszczenie: Spalanie odgrywa kluczową rolę w wielu procesach przemysłowych, takich jak ogrzewanie i wytwarzanie energii elektrycznej. Określenie wartości ciepła spalania dla różnych paliw jest istotnym krokiem w kierunku poprawy procesów spalania poprzez zwiększenie wydajności spalania lub zmniejszenie emisji. W pracy tej przedstawiono kalorymetr przepływowy Junkersa do wyznaczenia wartości ciepła spalania zarówno dla paliw czystych, jak i zmieszanych. Pomimo że metodologia zastosowana w badaniach własnych nie jest unikalna, uzyskane wyniki dostarczają wglądu w wartości ciepła spalania dla czterech różnych paliw – bioetanolu kukurydzianego, izopropylu, Bioseptolu 80, denaturatu oraz ich mieszanek. W rezultacie zaprezentowane badanie oferuje wgląd w wartości ciepła spalania dla różnych paliw, zapewnia ustandaryzowaną metodę pomiaru ciepła spalania, która może być wykorzystana do replikacji wyników oraz wskazuje główne czynniki mające wpływ na ich dokładność.

Słowa kluczowe: ciepło spalania, paliwo, mieszanka paliwowa, kalorymetria, spalanie

1. Introduction

Combustion is a highly exothermic reaction, which releases energy in the form of heat and light. It involves the reaction of fuel with an oxidant, typically oxygen, resulting in the production of carbon dioxide and water vapor.

Fuel combustion is a crucial process in many technical industries. For many years, the scientific community has realized that combustion reactions are often accompanied by negative effects, such as harmful pollutants or the risk of fire; however, we still benefit from the chemical energy contained in fossil fuels [9]. There are several reasons for this, including convenience, cost, and the high energy density of fossil fuels compared to the popular lithium-ion batteries. The energy density for gasoline is about 8.9 kWh/l [11], whereas for the 21700-type battery commonly used in electric cars and electric bicycles, the energy density ranges from 0.519 to 0.684 kWh/l [15]. Although such a comparison does not consider factors such as the efficiency of internal combustion engines and electric motors, it allows one to understand why the use of combustion to meet basic human needs is still common [4, 19, 20]. The heat of combustion is a key property that determines the energy content and efficiency of the fuel. Therefore, accurate measurements of the heat of combustion are essential for the development and optimization of clean and efficient energy technologies.

In this study, we aimed to determine the heat of combustion for a range of clean and mixed fuels by using a Junkers flow calorimeter. The study analyzes the change in the heat of combustion values after mixing fuels and compares the obtained results with the current scientific knowledge and observations made during the study.

The main purpose of this study was to measure the heat of combustion for a range of easily accessible, clean and mixed fuels including corn bioethanol, isopropanol, Bioseptol 80, and denatured alcohol. The study aims to verify the correctness of the used method and find the various factors responsible for the accuracy of the results obtained by using a Junkers flow calorimeter. With these conclusions taken into account, the study also aims to provide a clear and concise method of using the utilized type of calorimeter and an easier way of interpreting other results obtained with this method.

In summary, this study contributes to the understanding of the heat of combustion of clean and mixed fuels and one of the methods of measuring it using a Junkers flow calorimeter. The main conclusions of this study provide insights into the used method of measuring the heat of combustion.

2. Methodology

All measurements were performed using a Junkers flow calorimeter, as shown schematically in Fig. 1a, and photographed in Fig. 1b. A calorimeter was used to determine the lower heating values (LHV) of the fuel samples. Although the paper takes into account one burning of a sample, the results were verified by burning additional samples. It was determined that the noticed differences were smaller than the one that would be caused by the accuracy of the used devices, mainly the thermometer, thus the accuracy of the used devices was more crucial.

The calorimeter operates as follows: tap water enters the insulated Junkers flow calorimeter (1) through a flowmeter (2) and overflow vessel (3). The temperature T_1 is measured using the first thermocouple probe (4) of the thermometer (5). The water that flows into the water jacket (6) is heated by a sample burned immediately below the combustion chamber (7) in the fuel burner (8). A second thermocouple probe (9) measures the temperature T_2 of the heated, outflowing water indirectly by measuring the temperature of the pipe (10), which is in direct contact with the water.

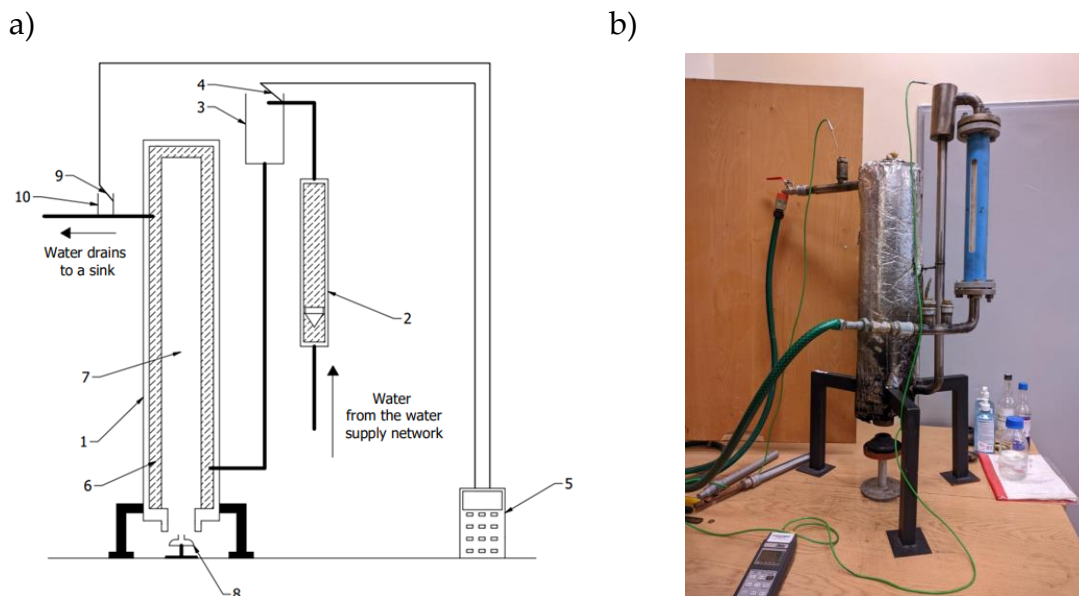


Fig. 1. a) Diagram of the Junkers flow calorimeter used to obtain the results;
b) the photograph of the Junkers flow calorimeter used to obtain the results (own study)

The following operating algorithm was used during the measurements:

1. The water flow rate in the calorimeter was measured using an RDN rotameter, a flowmeter produced by Zakład Automatyki Rotametr sp. z o.o connected to the calorimeter system. The accuracy of the rotameter was 0.5 l/h.
2. A known amount of fuel (10 ± 0.25 g) was injected directly into the fuel burner using a syringe. In the case of the mixed samples, both fuels were injected into the fuel burner in a known amount ($5 \text{ g} \pm 0.25$ g). The fuel was dosed using a Radwag WPS 210/C/1 laboratory balance, with an accuracy of 0.001 g.
3. For samples containing a mixture of fuels, the two fuels were mixed manually by shaking the fuel burner.
4. A fuel burner was positioned directly under the calorimeter along its axis so that the burning fuel could heat water flowing through the calorimeter.
5. The water temperatures at the inlet T_1 and outlet T_2 of the calorimeter were measured using a DO9416 thermometer with two thermocouple probes (Fig. 2) inserted into the inlet and outlet pipes of the calorimeter. The accuracy of the thermometer was 0.1°C .

a)



b)



Fig. 2. a) The first thermocouple probe of the DO9416 thermometer located at the inlet of the calorimeter in the overflow vessel, measuring the T_1 temperature;
b) the second thermocouple probe of the DO9416 thermometer located at the outlet of the calorimeter, measures the T_2 temperature (own study)

6. The difference between the two temperatures was treated as an error caused by imperfect insulation of the calorimeter. Therefore, T_1 was subtracted from T_2 during the calculations to reduce the error.

$$T_2 - T_1 = \Delta T \quad (1)$$

It is important to note that before the temperatures were measured, water flowed through the calorimeter for an hour which allowed the ΔT to stabilize and make it as small as possible.

7. The sample in the fuel burner was ignited using a gas lighter.
8. During the combustion of the sample, the temperatures T_1 and T_2 were measured every minute until the sample was completely burned and the temperature difference ΔT was equal to zero.
9. The heat flow rate was determined using the following equation:

$$\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T \text{ [W]} \quad (2)$$

where:

- $\dot{m}$ – mass flow rate [g/s],
- c_p – specific heat of water [$\frac{\text{J}}{\text{kg} \cdot \text{K}}$],
- ΔT – the difference between T_2 and T_1 [°C].

10. The energy E supplied to the water by the combustion process of the fuel sample was determined by integrating:

$$E = \int \dot{Q} \cdot dt \text{ [J]} \quad (3)$$

where:

- $\dot{Q}$ – the rate of heat flow [W].

11. The determined energy E was divided by the mass of the burned sample to determine the LHV in joules per gram of the burned fuel.
12. After converting the units, the LHV was obtained in the desired units, that is, megajoules per kilogram of fuel.

3. Materials

The types of fuels used in this study and their expected LHV were listed in Table 1. The samples from 1–4 were pure fuel. Samples 5–10 were obtained by mixing two pure fuels in a 1:1 ratio.

Table 1. Samples of fuels (own study)

Sample no.	Fuel	Composition	Expected LHV according to literature values and calculations [7, 8, 13] [MJ/kg]
1	63% corn bioethanol	ethanol 63%, water 37%	18.611 [12]
2	Bioseptol 80	ethanol (80–85%), isopropanol ($\leq 10\%$), cationic surfactant in the form of a mixture: didecyldimethylammonium chloride (50–60%), isopropanol (20–25%), 2-phenoxyethanol ($\leq 2\%$) [3]	18.5–23 Depending on the exact composition [5, 17]
3	Denatured alcohol	92% ethanol, methyl ethyl ketone, denatonium benzoate [14]	19–24.5 [5]
4	Isopropanol	Isopropyl alcohol	30.447–33.392 [6, 10]
5	63% corn bioethanol + Bioseptol 80	–	18.55–20.81
6	63% corn bioethanol + denatured alcohol	–	18.81–21.56
7	63% corn bioethanol + isopropanol	–	24.53–26
8	Bioseptol 80 + denatured alcohol	–	18.75–23.75
9	Bioseptol 80 + isopropanol	–	24.47–28.2
10	Denatured alcohol + isopropanol	–	24.72–28.95

Corn bioethanol is a biofuel produced by fermentation of corn sugar or starch. It is a renewable energy source that has the potential to reduce greenhouse gas emissions and dependence on fossil fuels. It can be used as a fuel additive or a standalone fuel in vehicles and industrial applications [1, 2, 18].

Bioseptol 80 is a disinfectant liquid solution containing 80–85% ethyl alcohol as its active ingredient and is effective against a wide range of microorganisms, including bacteria, viruses, and fungi. It is commonly used in healthcare settings and other

industries to prevent the spread of infections by killing or preventing the growth of microorganisms on surfaces or equipment. Bioseptol 80 can be applied through spraying, wiping, or soaking and is known for its fast-acting and broad-spectrum antimicrobial properties.

Denatured alcohol is an alcohol that has been treated with additives to render it unsuitable for human consumption. Denatured alcohol is commonly used as fuel for alcohol burners, stoves, and lamps, as well as for cleaning and disinfecting surfaces.

Isopropyl alcohol is a colorless and flammable chemical compound. It is commonly used as a disinfectant and antiseptic for cleaning wounds and as a solvent for various industrial and household applications. However, isopropyl alcohol should not be used as fuel in internal combustion engines because it can cause engine damage or failure [16].

4. Results and observations

Table 2. Summary of study results (own study)

Sample no.	Fuel	Sample mass [g]	Burning time [min]	Time until ΔT returned to initial state [min]	Highest ΔT [°C] $\pm 0,1$	Estimated LHV [MJ/kg]	Expected LHV acc. to literature values [MJ/kg]	Difference between expected and estimated LHV
1	63% corn bioethanol	10.003	28	34	0.8	16.78	18.611	9.84%
2	Bioseptol 80	10.152	24	34	0.9	17.68	18.5–23	14.8%
3	Denatured alcohol	10.140	21	23	0.6	8.89	19–24.5	59.13%
4	Isopropanol	10.058	32	56	0.9	24.82	30.447–33.392	22.24%
5	63% corn bioethanol + Bioseptol 80	10.171	27	32	0.8	14.78	18.55–20.81	33.15%
6	63% corn bioethanol + denatured alcohol	10.005	25	31	0.8	14.69	18.81–21.56	27.22%
7	63% corn bioethanol + isopropanol	10.236	24	37	1.0	20.31	24.53–26	19.61%
8	Bioseptol 80 + denatured alcohol	10.002	21	37	0.9	17.03	18.75–23.75	19.86%
9	Bioseptol 80 + isopropanol	9.865	26	32	0.5	13.60	24.47–28.2	48.36%
10	Denatured alcohol + isopropanol	9.991	26	32	0.5	10.53	24.72–28.95	60.76%

The estimated LHV values of all the samples were listed in Table 2. The discrepancies in the results indicate a lower value of the heat of combustion than expected, indicating the repeatability and accuracy of the adopted research method.

For sample 1 (bioethanol), the discrepancy in the determined LHV compared to the expected LHV was the lowest at 9.84%. The flame was regular, maintained its position, and showed no signs of combustion instability or significant fluctuations in the flame height. The sample burned after 28 minutes.

When sample 2 (Bioseptol 80) was burned, the discrepancy between the determined and expected LHV was 14.8%, which was the second smallest discrepancy. The flame was regular with a stable position. No signs of unstable combustion or significant fluctuations in flame height were observed. The sample was completely burnt after 24 minutes.

Sample 3 (denatured alcohol) had a large, second-largest discrepancy between the determined and expected LHV of 59.13%. This discrepancy correlates with the observations made during the combustion of the sample because the flame was irregular and unstable. The shape of the flame was indeterminate and had a chaotic structure; it did not maintain its position and its height fluctuated. It was blue and less visible than the flames of the other burned samples. The sample burned after 21 minutes, which was the shortest burning time, together with the eighth sample, which also contained denatured alcohol.

The discrepancy between the determined and expected LHV of sample 4 (isopropanol) was 22.24%. The flame was regular and stable during the sample combustion. No significant fluctuations in the flame height were observed. The sample burned for 32 minutes, which was the longest time among all tested fuels.

Sample 5 (bioethanol and Bioseptol 80) showed a discrepancy between the determined and expected LHV of 33.15%. The sample burned unevenly, there were fluctuations in its flame height, and its instability manifested as a failure to maintain a constant position. The combustion of the sample lasted 27 minutes. The determined LHV was lower than that of both fuels included and tested in a pure unmixed form.

Testing of sample 6 (bioethanol and denatured alcohol) yielded a discrepancy between the determined and expected LHV of 27.22%. The flame was characterized by a regular and stable position; during combustion, relatively small fluctuations in the flame height were observed. The combustion of the sample lasted for 25 minutes.

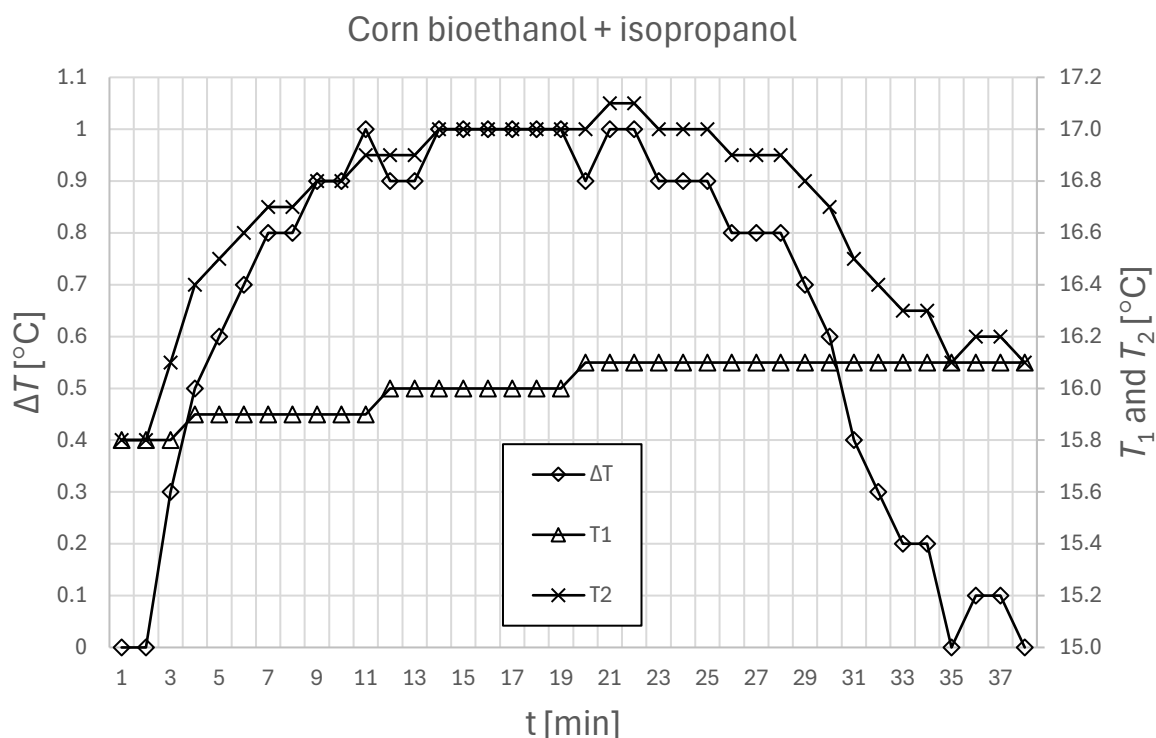


Fig. 3. ΔT , T_1 and T_2 temperatures during the combustion process of sample 7

In the burning of sample 7 (bioethanol and isopropanol), the discrepancy between the determined and expected LHV was 19.61%. The flame was regular and maintained its position, and no significant fluctuations in flame height were observed. During its combustion, the highest ΔT of 1°C was observed, as shown in Fig. 3. The sample burned in 24 minutes.

Sample 8 (Bioseptol 80 and denatured alcohol) showed a discrepancy between the determined and expected LHV of 19.86%. During the combustion of the sample, the flame was regular, and its position was maintained. The combustion of the sample ended after 21 minutes, which was the shortest combustion time among the samples, along with that of sample 3.

Sample 9 (Bioseptol and isopropanol) was characterized by a discrepancy between the determined and expected LHV of 48.36%. A significantly lower flame height, which was also relatively irregular, was observed during the combustion of this sample. No significant fluctuations in the flame height were observed during the combustion of the sample, which lasted for 26 minutes. The LHV determined for the sample was lower than that determined for both the components of the mixture in the pure form.

Sample 10 (denatured alcohol and isopropanol) had the largest discrepancy between the LHV and expected LHV of 60.76%. Low and fluctuating flame heights of irregular and unstable nature were also observed. The combustion of the final sample lasted for 26 minutes.

5. Discussion

The LHV was closest to those expected for samples 1 (bioethanol) and 2 (Bioseptol 80). The discrepancies were 9.84% and 14.8%, respectively. The remaining samples were characterized by a greater error ranging from 19.61% to 60.76%. The most problematic samples were those containing denatured alcohol, with samples 3 (denatured alcohol) and 10 (denatured alcohol and isopropanol), for which the discrepancy between the determined value and the expected value was 59.13% and 60.76%. During the combustion of samples 3 (denatured alcohol), 5 (bioethanol and Bioseptol 80), 9 (Bioseptol 80 and isopropanol), and 10 (denatured alcohol and isopropanol), a weak, unstable flame with variable height and blue coloration indicates a lower combustion temperature, which directly translates into a lower efficiency of the combustion process.

The highest experimentally obtained LHV (24.82 MJ/kg), was determined for sample 4 (isopropanol), which was consistent with the expected values. The lowest value was obtained for sample 3 (denatured alcohol), and the LHV was determined to be 8.89 MJ/kg. The expected value was as high as 19–24.5 MJ/kg.

All discrepancies indicate a lower-than-expected LHV, which demonstrates the peculiar repeatability of the results and the correctness of the adopted methodology. The errors are caused by the factors listed below, almost all of which underestimate the determined values, which correlates with the earlier observation that all determined values are lower than expected:

- The flame instability for samples 3, 5, 9, and 10 caused some heat not to enter the calorimeter but to escape it.
- Fluctuations in the height of the flame also caused it to be farther from the calorimeter; thus, more heat entered the surrounding environment instead of the inside of the calorimeter, where the flame would have heated the water.
- Fluctuating water temperature T_1 – for sample 4, as shown in Fig. 4 (isopropanol) there was a difference of as much as 0.6°C, which likely affected the results by artificially increasing the determined heat of combustion. Nevertheless, the error caused by fluctuating temperature T_1 during the testing of the fourth sample does not exceed ~10%.
- The thermometer used to measure temperatures T_1 and T_2 had an accuracy of 0.1°C which (with ΔT not exceeding 1°C) made up a relatively large error due to accumulating inaccuracies from measurements of temperatures T_1 and T_2 .
- The furnace was not in the axis of the combustion chamber – it was positioned manually on a flat stand, at a distance of several millimeters which meant that more heat than was possible entered the into the environment and not into the calorimeter to heat the water inside it.
- The furnace was not located in the combustion chamber but a few centimeters below it. Part of the heat will heat the furnace itself, and an even larger part of the heat will escape outside the calorimeter before it enters it.
- The calorimeter used for the test did not have perfect insulation, and the uninsulated pipes and rotameter had a relatively large surface area that was in direct contact with a warmer environment. Even after attempting to equalize the temperature by letting the water flow for several hours, ΔT did not drop below 0,3°C. An attempt was made to minimize this error as much as possible by subtracting

the initial value of ΔT from the value of T_2 before starting to burn the sample, nevertheless, the insulation certainly affected the results.

- The second thermocouple probe that measured the T_2 temperature was not in direct contact with the flowing water. It touched a pipe that was in contact with the flowing water. The heat inertia of the metal contributed to the delay in T_2 temperature changes, and thus affected the accuracy of the results.

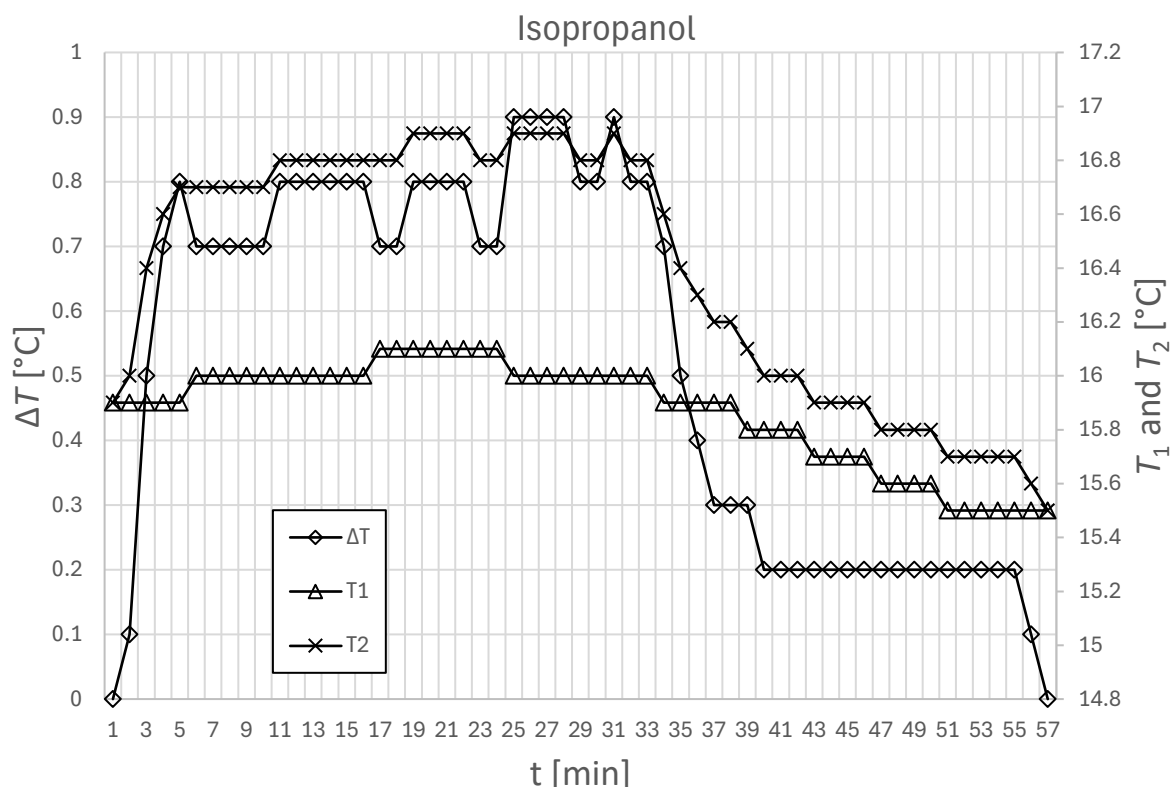


Fig. 4 ΔT , T_1 and T_2 temperatures during the combustion process of sample 4

In the case of the combustion of mixed samples, the fuels may not have been properly mixed as they were mixed manually by shaking the furnace, which may have negatively affected the fuel combustion process and certainly affected the flame properties observed during the combustion of each sample. This is directly related to the first factor mentioned, as flame instability was observed in 25% (1 of 4) of the pure fuel samples and 50% (3 of 6) of the mixed fuel samples.

In summary, the LHV for most samples (6 of 10) did not deviate from the expected value by more than 30%. The obtained results were satisfactory and most likely as accurate as possible, given the disadvantages of the type of calorimeter used for the study and the other aforementioned disruptive factors.

There is ample room for continuing studies of the heat of combustion of clean and mixed fuels. For example, it is possible to compare the values obtained using several types of calorimeters to determine the optimal measurement method for specific fuels. It is also possible to study the effect of ambient conditions on the results obtained and to study other fuel mixtures in different proportions, for example, in terms of heat of combustion and combustion efficiency.

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