WHITE PAPER

# The Importance of Testing for Accurate Energy Content of Biofuels

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## Introduction

Biofuels have the benefit of reducing greenhouse gas emissions as compared to conventional carbon-based marine fuels such as MGO, VLSFO and HSFO. However, the physical and chemical properties of biofuels vary considerably as compared to conventional fossil fuels. In addition, biofuels have more batch to batch and supplier to supplier variability as they are natural products. As a result, biofuels have several characteristics which need to be measured to mitigate operational problems when used on board sea-going vessels. VPS has carried out significant research across numerous parameters that enable these characteristics to be measured and controlled. VPS research has shown that by using these test methods, biofuels can be used as drop-in fuels on board vessels enabling the benefits of such fuels to be realised in the shipping sector.

This paper refers to energy content, which is an important parameter of a fuel as it represents the amount of heat transferred within the combustion chamber during the burn process and indicates the available energy of the fuel. Higher energy content results in higher power generation and better combustion efficiency. The energy content of the fuel has a direct impact on the fuel economy and therefore greenhouse gas emissions. This paper covers a range of fuel types, from 100% FAME (Fatty Acid Methyl Esters) through FAME blended with MGO, VLSFO and HSFO.

For conventional residual and distillate fuels, the energy content can be calculated within an acceptable degree of accuracy using a formula specified in an Appendix of the International Marine Fuel Standard ISO 8217. This paper compares data from a variety of fuel samples to correlate the calculated energy content (using Appendix H of ISO 8217:2017) with the measured energy content (using ASTM D240) of conventional fuels and FAME blends through to 100% FAME. The data shows that this correlation falls away at FAME content above 10%. This proves that the ISO 8217 calculation method cannot be relied upon to provide accurate energy content for fuel blends containing more than 10% FAME and that for these blends the accuracy of the calculation formula is not acceptable. This inaccuracy is due to the greater oxygen content of FAME (100% FAME varies ca. 10-15% oxygen content) as compared to conventional fuels (which typically contain very little oxygen). Furthermore, there is no calculation method available to calculate the energy content of biofuels accurately due to the variability of the oxygen content in the FAME.

**For blends containing more than 10% FAME, accurate assessment of energy content requires direct measurement using method ASTM D240.**

## Benefits of Knowing Accurate Energy Content for Ship Operators

Measuring the energy content in fuels is crucial for assessing fuel efficiency, managing operational costs, evaluating environmental impact, ensuring compliance, and maintaining engine performance and safety. It provides valuable information for ship operators to make informed decisions regarding fuel selection, consumption, and environmental responsibility, as detailed below:

**Fuel Efficiency:** Determining the energy content helps assess the fuel efficiency of different marine fuels. By comparing the energy content of various fuels, ship operators can make informed decisions regarding the most efficient fuel options. Higher energy content fuels can potentially provide more power per unit volume or weight, resulting in improved vessel performance and reduced fuel consumption.

**Operational Costs**: Energy content measurement directly affects the cost of operating a vessel. Fuel costs constitute a significant portion of the operational expenses for shipping companies. Measuring the energy content allows for accurate calculations of fuel consumption and cost estimates, enabling effective budgeting and financial planning.

**Emissions and Environmental Impact**: The energy content of marine fuels is closely linked to the amount of carbon dioxide ($CO_2$) and other greenhouse gas emissions produced during combustion. By measuring energy content, it becomes possible to estimate the emissions footprint of a vessel. This information is critical for compliance with environmental regulations and for monitoring and reducing emissions to mitigate the impact of shipping on climate change.

**Fuel Quality and Characteristics**: Energy content measurement helps ensure the quality and performance of marine fuels. International standards and regulations, such as the ISO 8217 standard for marine fuels, set specific methods for calculating the energy content. Accurate measurements are required to detect any discrepancies, such as diluted or contaminated fuels, preventing potential operational and commercial issues or damage to ship engines.

**Performance and Safety**: The energy content of marine fuels directly affects engine performance and safety. Engines are designed to operate optimally within specific energy ranges. Knowing the energy content helps ship operators ensure that the fuel being used matches the engine's requirements, preventing issues such as poor combustion, reduced power output, or potential engine damage.

## Methods to Determine Energy Content in Marine Fuels

The standard test method for accurately measuring energy content in fuel is via a bomb calorimeter (ASTM D240 - Standard Test Method for Heat of Combustion of Liquid Hydrocarbons by Bomb Calorimeter). For marine fuels, a calculation method for specific energy is described in the Appendix of ISO 8217 (Appendix H of ISO 8217:2017), which helpfully explains the limitation of accuracy of this method. Both the ASTM D240 and ISO 8217 methods are detailed in the Appendix of this paper. For information, Gross Specific Energy (GSE) referred to in ISO 8217 is the same as Gross Calorific Value (or Gross Heat of Combustion) in ASTM D240 and Net Specific Energy (NSE) referred to in ISO 8217 is the same as Net Calorific Value (Net Heat of Combustion) in ASTM D240.

It is important to understand the difference between 'Gross' and 'Net' energy content. During fuel combustion, the oxidation of hydrogen in hydrocarbon fuels produces water, which escapes through the exhaust in a diesel engine. To compensate for this loss and to measure the useful energy produced during fuel combustion, Net Energy Content is calculated and reported rather than Gross Energy Content. Definitions for Gross and Net energy content are provided in the Appendices.

This paper sets out to study how various levels of FAME present in biofuels can affect the accurate determination of energy content of the fuel. A key consideration of the impact of FAME content in biofuel blends is the changing chemistry driven by a change in the oxygen content, as illustrated in Table 1 below.

**Table 1 Analysis results on Diesel fuels *(From Concawe environmental science for the European refining industry Courtesy report 6/14)***

| Fuel Property | Units | Test Method | B0 | B10 | B30 | B50 |
|---|---|---|---|---|---|---|
| Carbon | % m/m | ASTM D5291 | 85.84 | 84.97 | 82.99 | 81.11 |
| Hydrogen | % m/m | ASTM D5291 | 13.73 | 13.50 | 13.20 | 12.84 |
| Oxygen | % m/m | ASTM D5291 | 0.04 | 1.1 | 3.3 | 5.4 |
| Energy Content | MJ/kg | ASTM D240/IP12 | 42.89 | 42.32 | 41.22 | 40.06 |

## Methodology Applied to Compare Different Methods of Determining Energy Content

A number of conventional fossil fuels encompassing marine fuel types HFO, VLSFO and MGO were tested using method ASTM D240 and the energy content compared with that calculated using ISO 8217 calculation method. This work was then repeated for a number of biofuel samples with varying FAME content. Analysis of the results obtained for each of these different fuel types is detailed in the sections below. The results are illustrated graphically in Figures 1, 2, 3 and 4 and the correlation is summarised in Table 2.

These results show good correlation for conventional fuels, indicating that the ISO8 217 calculation method provides an acceptable degree of accuracy for measuring energy content in conventional fuels. However, for biofuels with FAME content greater than 10%, accurate energy content can only be determined by measurement using calorimetry.

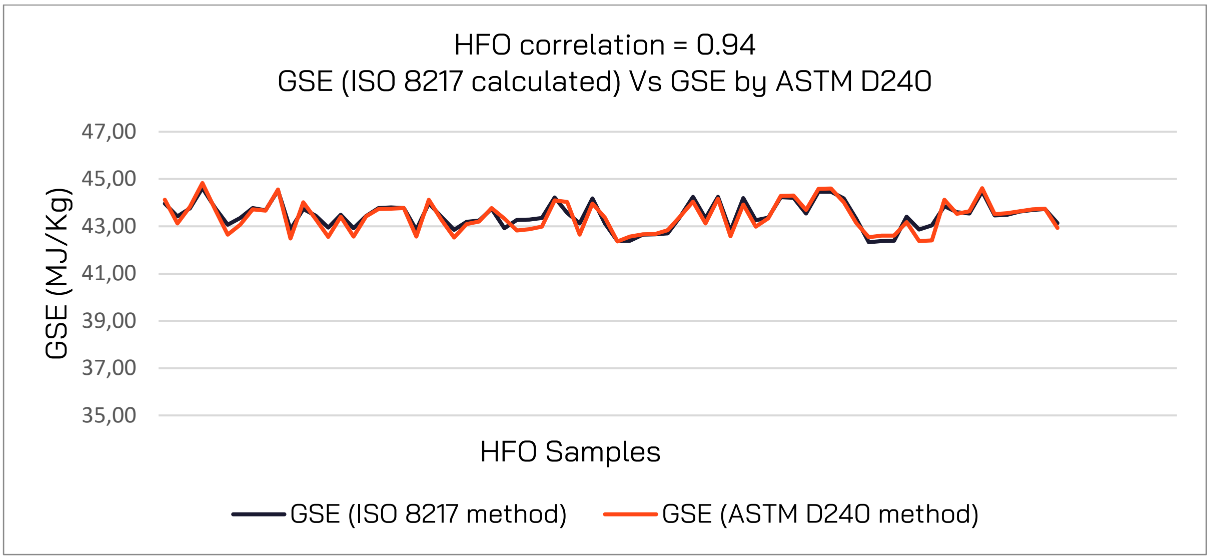
**Table 2 Correlation of GSE Determination by ISO 8217 Calculation Versus Measurement by Calorimetry (ASTM D340)**

| Fuel Type | Correlation of GSE by ISO 8217 Calculation Vs Measurement by Calorimetry |
|---|---|
| HFO | 0.94 |
| MGO | 0.92 |
| VLSFO | 0.89 |
| Biofuel (0-100% FAME) | 0.62 |
| Biofuel (>10% FAME) | 0.33 |
| Biofuel (<10% FAME) | 0.87 |

## Comparison of Energy Content of HFO Samples

A number of HFO samples (72) were tested by ASTM D240 to measure the GSE and this was correlated with the GSE determined by the ISO 8217 calculation method. This correlation is graphically illustrated in Figure 1 and the correlation coefficient has been measured as 0.94 (indicating very good correlation).

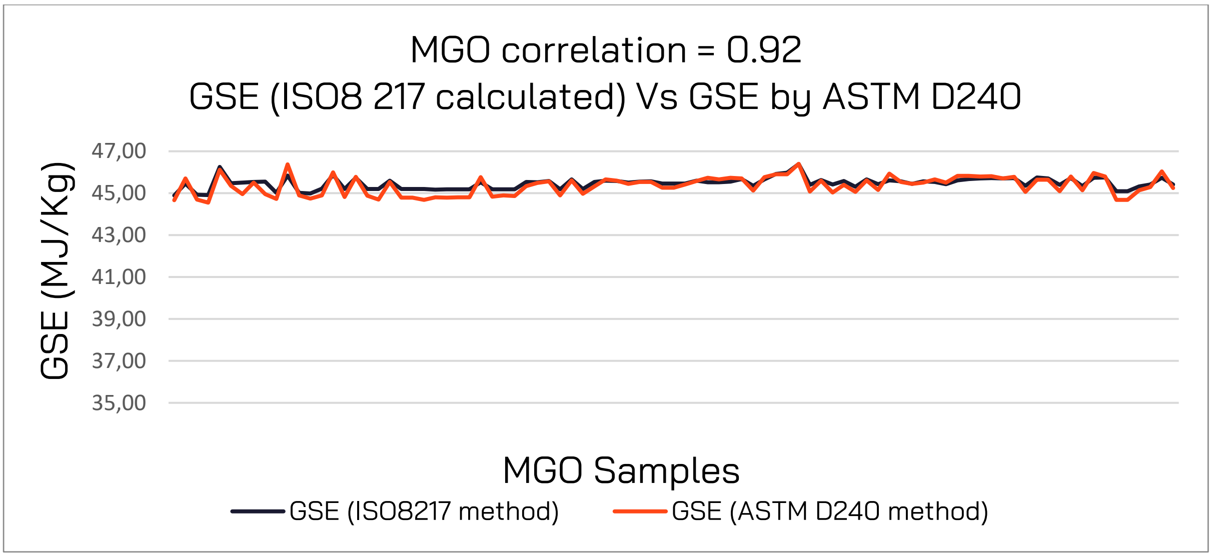
**Figure 1: GSE analysis of HFO samples using ISO 8217 calculation method and ASTM D240**



## Comparison of Energy Content of MGO Samples

A number of MGO samples (89) were tested by ASTM D240 to measure the GSE and this was correlated with the GSE determined by the ISO 8217 calculation method. All samples in this correlation contained <10% FAME. This correlation is graphically illustrated in Figure 2 and the correlation coefficient has been measured as 0.92 (indicating very good correlation).

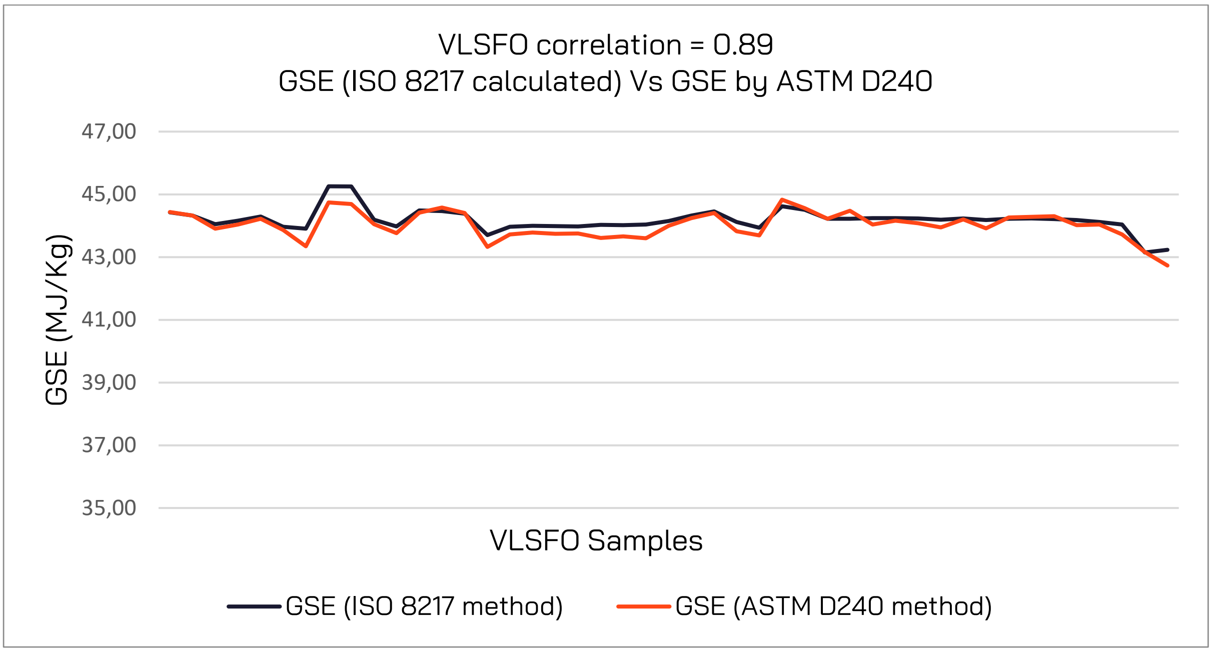
**Figure 2: GSE analysis of Distillate samples using ISO 8217 calculation method and ASTM D240**



## Comparison of Energy Content of VLSFO Samples

A number of VLSFO samples (47) were tested by ASTM D240 to measure the GSE and this was correlated with the GSE determined by the ISO8 217 calculation method. This correlation is graphically illustrated in Figure 3 and the correlation coefficient has been measured as 0.89 (indicating good correlation).

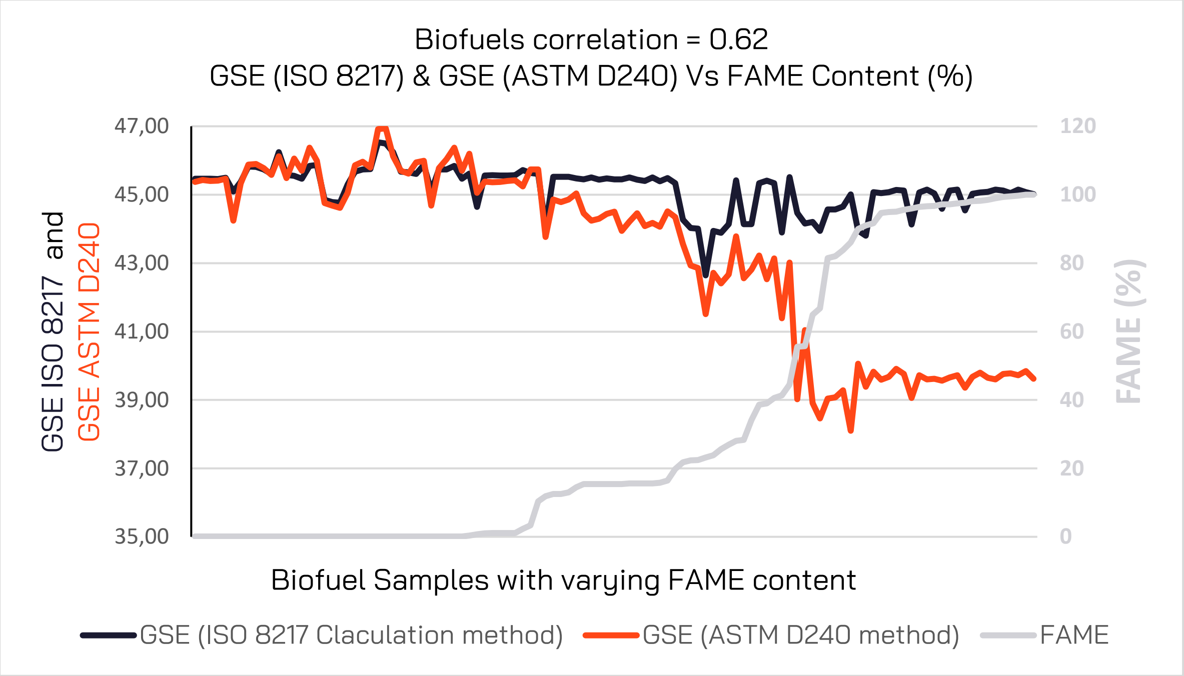
**Figure 3: GSE analysis on VLSFO samples using ISO 8217 calculation method and ASTM D240**



## Comparison of Energy Content of Biofuel Samples

A number of biofuel samples (112) were tested by ASTM D240 to measure the GSE and this was correlated with the GSE determined by the ISO8 217 calculation method. This correlation is graphically illustrated in Figure 4 and the correlation coefficient has been measured as 0.62 (indicating poor correlation).

**Figure 4: GSE analysis on Biofuels of varying FAME content using ISO 8217 calculation method and ASTM D240**



In order to investigate this correlation further, this group of biofuel samples were split into two groups, one less than 10% FAME content and the other greater than 10% FAME content. For the biofuel samples <10% FAME (46) the correlation coefficient has been measured as 0.87 (indicating good correlation). For the biofuel samples >10% FAME (66) the correlation coefficient was measured as 0.33 (indicating very poor correlation). For biofuel samples >96.5% FAME (16) the correlation coefficient was measured as 0.69 (indicating very poor correlation). This demonstrates that the ISO 8217 method of calculating GSE is inaccurate for biodiesel samples containing >10% FAME.

## Summary

The calorific value of Biofuels is lower than conventional petroleum-based diesel fuels. VPS statistics from various samples tested during 2020 to 2023 indicate an average 12% reduction in the energy content of Biodiesels as compared to VLSFO. This is because Biofuels contain FAME which has a higher amount of oxygen as compared to the conventional petroleum-based fuels. An increase in FAME content shows a subsequent decrease in calorific value.

The analysis carried out in the above paper concludes that the empirical formula for measuring energy content stated in ISO 8217 is not suitable for fuels containing FAME, such as Biodiesel. This is because the empirical formula does not account for oxygen present in FAME and is only based on the linear relationship between density and energy content.

ASTM D240 method covers the determination of energy content in distillate and residual fuels using Bomb calorimeter. Analysis shows that ASTM D240 is a suitable method for Biodiesel containing FAME.

Based on the analysis study carried on various Biofuels with varying FAME content currently being supplied (2020-2023), a linear relationship between the FAME (%) and the energy content could not be established mainly because the FAME and the oxygen in the FAME are both variables.

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## Appendix 1 - Determination of Energy Content using Method ASTM D240

This method covers the determination of heat of combustion of liquid hydrocarbon fuels ranging from distillates to residual fuels. Heat of combustion is determined in this test method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions.

The bomb is usually made of stainless steel and the combustion takes place at constant volume and there is no work done. Thus, there is no change in internal energy.

Heat of combustion is calculated from temperature observations before, during and after combustion. This is computed with heat of combustion of standard benzoic acid caid of known calorific value.

The heat released from the fuel during the combustion is the calorific value of the fuel. Since this method involves the actual combustion of fuel at constant volume (i.e. close to an adiabatic process), it can measure tiny energy changes and can be considered more accurate as compared to other empirical methods. During combustion process the oxidation of hydrogen in hydrocarbon fuels produces water.

$$2H_2 + O_2 \rightarrow 2H_2O$$

The result from this test gives the gross heat of combustion as it includes the heat of vaporisation of the water that is produced during the combustion process.

Considering the typical combustion process in a diesel engine the water vapour escapes through the exhaust and is not used. To compensate for this loss and to estimate the useful energy, the Net Heat of Combustion also known as the Net Calorific Value (NCV) can be calculated by subtracting the latent heat of vaporisation from the gross heat value but for this we need to know the hydrogen content in the fuel. Hydrogen content can be determined using ASTM D5291 and Net Calorific Value can be calculated as follow:

Net Calorific Value = Gross Calorific Value – 0.2122 x Hydrogen.

## Appendix 2 – Calculation Method ISO 8217

For conventional residual and distillate fuels such as VLSFO, HFO and Distillate fuels the NCV and GCV both are expressed in megajoules per kilogram and can be calculated with a degree of accuracy acceptable for normal purposes. The equation used for calculation as stated in ISO 8217 is stated below:

Residual fuels

$Q_{Rnp}$- *Net specific energy*

$$Q_{Rnp} = (46.704 - 8.802[\rho 15]^2.10^{-6} + 3.167\rho 15.10^{-3}).[1 - 0.01(w_w + w_a + w_s)] + 0.0942.w_s - 0.02449.w_w$$

$Q_{Rgv}$- *Gross specific energy*

$$Q_{Rgv} = (52.190 - 8.802[\rho 15]^2.10^{-6}).[1 - 0.01(w_w + w_a + w_s)] + 0.0942.w_s$$

Distillate fuels

$Q_{Dnp}$- *Net specific energy*

$$Q_{Dnp} = (46.423 - 8.792[\rho 15]^2.10^{-6} + 3.170\rho 15.10^{-3}).[1 - 0.01(w_w + w_a + w_s)] + 0.0942.w_s - 0.02449.w_w$$

$Q_{Dgv}$- *Gross specific energy*

$$Q_{Dgv} = (51.916 - 8.792[\rho 15]^2.10^{-6}).[1 - 0.01(w_w + w_a + w_s)] + 0.0942.w_s$$

Where:
$\rho 15$ - is the density at 15 °C, expressed in kilograms per cubic metre;
$w_w$ - is the water content, expressed as a mass percentage;
$w_a$ - is the ash content, expressed as a mass percentage;
$w_s$ - is the sulfur content, expressed as a mass percentage.

The empirical formula can calculate the energy content of a fuel to a good degree of accuracy. This is due to the empirical linear relationship between density and energy content of fuels. However, this relationship does not hold good when the fuel contains oxygenated compounds such as FAME in Biodiesel. This is because the above empirical formula does not account for the oxygen present in FAME.

Unlike conventional fuel, Biofuel can contain FAME. Depending on the blend the FAME concentration could significantly vary (0 to 100%). Additionally, the oxygen content in FAME from one source can significantly vary from another. Due to these reasons, it is appears impractical to derive an empirical formula for calculating the calorific value of Biofuel that contains FAME.

## Appendix 3 – Definitions of Gross Calorific Value/Gross Specific Energy and Net Calorific Value/Net Specific Energy

The Gross Calorific Value (GCV) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C and latent heat of vaporization of water is recovered by condensation of water vapor in the combustion products.

The GCV is same as Gross Specific Energy (GSE) referred in the ISO 8217. The Net Calorific Value (NCV) of a fuel is defined as the amount of heat released by combusting a specified quantity of fuel (initially at 25°C) in oxygen with all of the products being gaseous and in which the latent heat of vaporization of water in the reaction products is not recovered (water remains as vapor).

The NCV is the same as Net Specific Energy (NSE) referred in the ISO 8217.