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Petroleum products — Calculation of specific energy of residual fuels from physical and compositional properties — Basic data

*Produits pétroliers — Calcul de l'énergie spécifique des combustibles
résiduels à partir de caractéristiques physicochimiques et d'éléments de
composition — Données de base*



Contents

1 Scope 1

2 Data analysis approach..... 1

3 Definitions 1

4 Data analysis 2

4.1 Verification of Cragoe analysis 2

4.2 Simplified equation..... 3

5 Net specific energy 4

5.1 Cragoe relationships 4

5.2 Verification of the Cragoe relationship..... 5

5.3 Simplified equation..... 5

6 Conclusions 6

Annex A (informative) Raw data for specific energy calculations..... 7

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

- type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;
- type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;
- type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard (“state of the art”, for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until data they provide are considered to be no longer valid or useful.

ISO/TR 18455, which is a Technical Report of type 3, was prepared by Technical Committee TC 28, *Petroleum products and lubricants*.

Annex A of this Technical Report is for information only.

Introduction

Knowledge of the specific energy of residual fuel oils is important for both fuel choice and end-use design and operation. Measurement of this property is time-consuming, requires specialist skills, and does not lead to great precision. Thus for many years, specific energy values have been derived for general use by calculation from other determined properties.

This Technical Report gives the basic data and the derivation of equations widely used in the petroleum industry for the estimation of specific energy of residual fuels. The following International Standards use equations developed from the data given in this Technical Report:

ISO 4261:1993, *Petroleum products — Fuels (class F) — Specifications of gas turbine fuels for industrial and marine applications*.

ISO 8217:1996, *Petroleum products — Fuels (class F) — Specifications of marine fuels*.

Detailed compositional analysis, or even simple physical separation, is not often possible on residual fuel oils because of their nature. Thus the techniques applied to calculations of specific energy of gases and distillate petroleum products are not applicable to residual fuel oils. The first empirical approach to the problem was published by Cragoe in 1929¹⁾. Subsequent methods of calculation have been based on the same basic principle — that the specific energy can be related to the density of the product, with adjustment for the compositional variables of water, sulfur and ash content.

The Cragoe formulae were used almost exclusively in the petroleum industry until the 1960's. It was then realized that this relationship was based on residual fuels blended exclusively from components manufactured by straight-run refinery processes, together with crude petroleum and petroleum products. It was suggested that the newer processing routes for residual fuels emerging at this time, and the fact that the Cragoe formulae were based on a wide cross-section of fuel and crude petroleum types, could influence the factors in the equations if restricted to a single residual fuel group. Also outside the US, there was a growing need for a modern metric equivalent of the Cragoe formulae. New formulae were developed by many standardization bodies during the period 1966 to 1974, and these largely gave a very small change to the calculated value of specific energy of residual fuel oils.

By the late 1970's, severe processing of residues was becoming more commonplace. More significantly, skill levels and staff numbers were declining in petroleum laboratories. Since any empirical formula or equation is essentially a regression analysis of determined data to achieve a best fit relationship expressed as an equation, it is essential that both the determined analyses are on a representative sample of the whole population, and that they have a high level of technical integrity. It was thus decided that a large-scale exercise to derive a relationship representative of world-wide residual fuel oil availability should be carried out, probably for the last time possible. French experts from Bureau de Normalisation du Pétrole (BNPé) were asked to carry out this work, and in the process, to verify that the original Cragoe relationship still applied across the residual fuel oil types then currently available. The work was carried out during 1980 and 1981, and reported in December 1981²⁾.

¹⁾ Cragoe, US Bureau of Standards, Miscellaneous Publication No. 97, November 1929.

²⁾ Report of Experts from France, December 1981.

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1 Scope

This Technical Report looks at data from 258 samples of residual fuel oil on which specific energy has been determined by the standard technique of bomb calorimeter by experienced technicians. For 15 of these results, there was insufficient physical and/or chemical data to calculate a corresponding value. In many cases, the values reported for water content were lower than the reporting limit (0,05 % or 0,10 %), and in some cases, this also applied to ash content. This Technical Report also contains much hydrogen content data, both measured and calculated. The residual fuel oils examined cover a range of density at 15 °C from 912 kg/m³ to 1 032 kg/m³, and are estimated to cover all the major crude petroleum source regions and normal petroleum processing options available in the late 1970's. The sulfur contents range from 0,33 %(*m/m*) to 5,19 %(*m/m*). No samples of high water content or high ash content were included in this analysis.

NOTE 1 For the purposes of this Technical Report, the terms '%(*m/m*)' and '%(*V/V*)' are used to represent the mass and volume fractions respectively.

2 Data analysis approach

The approach taken in this Technical Report was to firstly verify that the Cragoe approach to gross specific energy calculation was valid for this data set, then to look at the numerical values in the Cragoe formulae, and adjust them as necessary to provide a best fit relationship, and finally to examine the relative importance of individual components of the Cragoe formulae, to provide simplified equations of acceptable precision.

During this process, a number of generalizations were highlighted, and although these are likely to give a negligible bias to calculated results in this data set, absolute accuracy would demand a detail of analysis not present generally for residual fuel oils. These generalizations largely relate to the fact that specific energy is a function of the hydrocarbon composition of the material under examination, with a very small adjustment for sulfur, whereas the bulk properties are measured on the whole sample. These effects are likely to be greater in the calculation of net specific energy, where Cragoe uses a direct relationship between hydrogen content and density, but even here, the effects are extremely small. There are also slight anomalies in the reporting of water content, where both '%(*m/m*)' and '%(*V/V*)' are possible, and generally not identified. Again, because water contents in this data set are low, and densities are close to 1 000 kg/m³ at 15 °C, the effect can be regarded as negligible.

Finally, a slight complication to the data analysis is the fact that Cragoe used Imperial units for all his calculations, specifically in terms of density (where he used relative density at 60/60 °F), and units of report (where he used BtU/lb, BtU/USG and cal/g). Conversion to SI units, whilst not difficult, does introduce the potential for error. In actual practice, this Technical Report continues this trend, in that the original document produced by the French experts expressed density in terms of kg/l, whereas all ISO documents since the early 1980's have used the correct SI unit of kg/m³. This latter unit is now widely accepted in the petroleum industry, and is used in this Technical Report.

3 Definitions

For the purposes of this Technical Report, the following definitions apply:

3.1**gross specific energy**

total quantity of heat released by combustion of a unit mass of fuel with oxygen saturated with water vapour at constant volume. The reactants and combustion products are considered at the same temperature, with the water produced in the liquid phase.

3.2**net specific energy**

quantity of heat released by combustion of a unit mass of fuel with oxygen under a constant pressure of 101,3 kPa. The water formed during combustion remains in the vapour phase. The net specific energy is the gross specific energy less the latent heat of the water produced during combustion.

NOTE 2 The obsolescent terms 'calorific value' or 'heat of combustion' will be found in the references contained in this Technical Report.

4 Data analysis**4.1 Verification of Cragoe analysis****4.1.1 Cragoe equations for gross specific energy**

The Cragoe relationships for the heavier petroleum products were based on an analysis of experimental data on 630 'petroleum oils' from 11 countries, analyses being carried out by five 'groups of observers'. By implication, these 'petroleum oils' included kerosines, distillate fuel oils, residual fuel oils and crude petroleum, and ranged in density from approximately 780 kg/m³ to 1 000 kg/m³. Sub-groups of this data set do not appear to have been analyzed.

Cragoe derived a series of relationships which were all based on the discovery that the gross specific energy of the hydrocarbon portion of a crude petroleum or petroleum product bore a constant relationship to the relative density, of the form:

$$Q_s = 12\,400 - 2\,100r^2 \quad (1)$$

where

Q_s is the gross specific energy of the hydrocarbon part of the material, in calories per gram;

r is the relative density at 60/60 °F.

From this relationship, the gross specific energy of the complete petroleum material could be expressed as:

$$G = Q_s - 0,01Q_s(w + a + s) + 22,5s \quad (2)$$

where

G is the gross specific energy of the whole material, in calories per gram;

w is the percentage by mass of water;

a is the percentage by mass of ash;

s is the percentage by mass of sulfur.

The factor 22,5, derived by Cragoe for the specific energy of sulfur, is a compromise figure based on an 'average' sulfur compound. It is likely to be low for the lighter compounds and high for the heavy compounds where sulfur is in complex large molecules.

Translation of these equations into the SI units of megajoules per kilogram (MJ/kg) for specific energy and kilograms per cubic metre for density at 15 °C (ρ_{15}) gives: