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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

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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 Technical Reports of type 3 do not necessarily have to be reviewed until data they provide are considered to be no longer valid or useful.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 1929[1]. 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 1981[2].

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

[2] Report of Experts from France, December 1981.

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

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/m^3 to 1 032 kg/m^3, 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/m^3 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/m^3. 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/m^3 to 1 000 kg/m^3. 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:

$$Q_s = 12\,400 - 2\,100 r^2 \tag{1}$$

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:

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

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:

$$Q_s = 51{,}900\ 2 - \left[8{,}802 \left(\rho_{15}^2 \times 10^{-6} \right) \right] \tag{3}$$

$$G = Q_s - 0{,}01 Q_s \left(w + a + s \right) + 0{,}094\ 2s \tag{4}$$

where

51,900 2   is 12 400 x 4,185 5 x 10⁻³;

8,802   is 2 100 x (0,999 7/0,999 012)² x 4,185 5 x 10⁻³;

0,999 7   is the coefficient of conversion from density at 60 °F to density at 15 °C;

0,999 012 is the coefficient of conversion for the change in density of water between 60 °F and 15 °C;

0,0942   is (22,5) x (4,185 5) x (10⁻³).

NOTE 3   The figures of 0,999 7 and 0,999 012 are derived using ITPS 68, the International temperature scale extant in 1981, when the French expert's report was published. Using ITS 90, the current scale, these figures are changed in the fourth and sixth decimal place respectively, and this has a consequent very small effect on the figure of 8,802. Since the figure of 4,185 5 for the mechanical equivalent of heat used by the French experts is also marginally suspect, the actual factors in this equation (4), and the others derived from it, are not mathematically exact from the third decimal place. However, firstly this Technical Report is a reflection of the report submitted by the French experts, and accepted by ISO/TC 28/SC 4/WG 5 and WG 6, and not a re-analysis of the data. Secondly, any changes to factors in the equations at this sensitivity has no practical effect on their usable value, as they are comfortably within any reasonable rounding margins.

4.1.2 Relative importance of Cragoe factors

For a typical residual fuel oil with a density of 990 kg/m³ at 15 °C, a sulfur content of 3,8 %(m/m), a water content of 0,1 %(m/m) and an ash content of 0,04 %(m/m), equation (3) gives a value for Q_s of 43,27 MJ/kg. The sulfur adjustment decreases this value by approximately 3 %, and the water and ash contents reduce the value by a further 0,14 %, giving a final gross specific energy of 41,93 MJ/kg. It can thus be concluded that in the absence of significant contamination by water or mineral matter, the determination of density and sulfur content will give an estimated gross specific energy accurate enough for most practical applications.

4.1.3 Verification of Cragoe relationship

The data given in annex A include experimental values of gross specific energy, density and sulfur content, and in most cases, experimental values of water and ash contents. Where available, the table includes both determined and calculated figures for hydrogen content, and for just over 50 % of the samples, a determined figure for carbon content. The table then gives a value for gross specific energy derived from the Cragoe equation (4), and a difference between this value and the determined value.

The results show that in 98 % of cases, the calculated result from the Cragoe equation for gross specific energy is within 2 % of the determined value, with a distinctive bias towards a lower figure for the calculated figure. This bias has an average value of 0,28 MJ/kg. Examination of the sub-groups within the sample matrix shows that the bias is constant for sub-groups based on either sulfur content, crude petroleum source area or processing route. In physical terms, the bias does not appear to relate to either density or viscosity.

It thus appears that a small correction to the factors in the Cragoe formulae will result in a relationship that is valid for the residual fuel oils examined, and by extrapolation, for the residual fuel oil market in the early 1980's, and hopefully beyond.

Examination of the best fit relationship shows that the factors in equation (3) should both be changed, but that a change of the factor 51,900 2 to 52,190 suffices to meet all statistical criteria for correlation, and this is the route adopted.

4.2 Simplified equation

Having verified the Cragoe approach, and made a minor modification to the relationship, it is possible to produce a simplified form of the equation for practical usage, as discussed in 4.1.2. In addition to discarding the water and ash

content, a further simplification can be introduced by substituting '$\rho_{15}^2 \times 10^{-6}$' by '$(2\rho_{15} - 1\,000) \times 10^{-3}$' on the basis that residual fuel oils will have densities close to 1 000 kg/m³ at 15 °C. To one decimal place, Q_s then becomes:

$$Q_s = 61{,}0 - 17{,}6\left(\rho_{15} \times 10^{-3}\right) \tag{5}$$

Adding the correction for sulfur $(-Q_s/100 + 0{,}094)s$, with a density of 1 000 kg/m³ substituted in equation (5), the simplified equation becomes:

$$G = 61{,}0 - 17{,}6\left(\rho_{15} \times 10^{-3}\right) - 0{,}34s \tag{6}$$

For the samples described in annex A, this equation gives a very high correlation, but as mentioned previously, these samples had low water and ash contents, and confidence will be subject to this provision. In general however, for samples with higher water contents, a simple adjustment (subtraction) for the water content is easy to perform, and this simplified equation will still give a rapid estimation of the gross specific energy.

5 Net specific energy

5.1 Cragoe relationships

The construction of similar equations for the calculation of net specific energy requires the subtraction of the latent heat of vaporization of water.

Cragoe, in his calculations, used simplified empirical factors which have been shown to give good relationships, bearing in mind the precision of measurement of hydrogen content, which is discussed later. The first step of Cragoe was to again look at the hydrocarbon portion of the material, and work from the same gross specific energy figures discussed in 4.1.1. On this basis, the net specific energy, N_p, in calories per gram, becomes:

$$N_p = Q_s - 0{,}01H\left(\left[9 \times 585\right] - 220\right) \tag{7}$$

where

    H is the percentage by mass of hydrogen in the hydrocarbon;

    585   is the latent heat of evaporation of water, in calories per gram at 20 °C;

    220   is a correction for the change in volume between initial and final phases;

    9   is a coefficient of transformation of the percentage mass of hydrogen into percentage mass of water.

Cragoe then connected the percentage mass of hydrogen to the relative density at 60/60 °F using the equation:

$$H = 26 - 15r \tag{8}$$

Thus, for the hydrocarbon portion of the material, the net specific energy could be expressed as:

$$N_p = Q_s - 50{,}45(26 - 15r) \tag{9}$$

Applying this equation to the actual material under examination by correcting for water, ash and sulfur contents, the Cragoe relationship for net specific energy, N_a, in calories per gram, became:

$$N_a = N_p\left[1 - 0{,}01(w + a + s)\right] + 22{,}5s - 5{,}85w \tag{10}$$

Conversion of this equation into SI units gives the relationship:

$$N_a = \left\{46{,}704 - \left[8{,}802\rho_{15}^2 \times 10^{-6}\right] + \left[3{,}167\left(\rho_{15} \times 10^{-3}\right)\right]\right\} \times \left[1 - 0{,}01(w + a + s)\right] + 0{,}094\,2s - 0{,}024w \tag{11}$$

5.2 Verification of the Cragoe relationship

The calculation of net specific energy is based on the same value of gross specific energy as has already been verified in 4.1.3, plus the empirical relationship between hydrogen content and relative density at 60/60 °F developed by Cragoe, and given in equation (8).

If we assume that the water content and ash content are negligible, then:

$$H_p = H_a / 1 - 0{,}01s \tag{12}$$

and

$$H_a = \frac{26 - 15{,}01\left(\rho_{15} \times 10^{-3}\right)}{1 + 0{,}01\,s} \tag{13}$$

where

H_p is the hydrogen content of the hydrocarbon portion of the material, in percentage by mass;

H_a is the hydrogen content of the actual material, in percentage by mass;

15,01 is 15 times the conversion factor for relative density at 60/60 °F to density at 15 °C.

The results of 217 hydrogen contents are given in annex A, with both experimental values obtained by elemental analysis, and calculated values obtained from equation (13). These show that in 77 % of cases, the difference between determined and calculated value is less than 5 % of the measured value, in 92 % of cases, this difference is less than 7,5 %, and in 98 % of cases, this difference is less than 10 %. The mean systematic error, obtained by dividing the algebraic sum of the absolute variations by their number, is 0,06, a value which is negligible when compared to the values being considered, and thus the mean is considered to be well-centred, and no corrections to empirical coefficients are necessary.

Thus we can conclude that since the new empirical relationships for the determination of gross specific energy gives 95 % of results within 1,4 % of the measured value, and the empirical relationship for hydrogen content gives 95 % of results within 8,5 % of the measured value, mathematical analysis concludes that 95 % of calculated results for net specific energy will be within 2 % of the measured value.

5.3 Simplified equation

In the same manner as for gross specific energy (4.2), a simplified relationship can be developed for net specific energy. The simplified relationship based on the Cragoe approach yields:

$$N_a = 55{,}5 - 14{,}4\left(\rho_{15} \times 10^{-3}\right) - 0{,}32s \tag{14}$$

A similar simplified relationship, attributed to Marder, had different coefficients, as follows:

$$N_a = 52{,}9 - 11{,}9\left(\rho_{15} \times 10^{-3}\right) - 0{,}29s \tag{15}$$

The difference in result from the usage of these two equations on typical high-sulfur residual fuel oils is negligible for practical purposes.

6 Conclusions

6.1 The current analysis of over 250 data sets on a wide variety of residual fuel oils available from 1979 to 1981 showed that the traditional Cragoe relationships are still valid for the calculation of gross specific energy and net specific energy. Small adjustments to the coefficients in the original equation for gross specific energy are proposed to provide a better fit for these current materials in this class. The equation for net specific energy remains unchanged.

6.2 The equation for gross specific energy, *G*, in megajoules per kilogram, is proposed as:

$$G = Q_s - 0,01 Q_s (w + a + s) + 0,094\ 2s$$

where

$$Q_s = 52,190 - \left[8,802 \left(\rho_{15}{}^2 \times 10^{-6} \right) \right]$$

In full, this equation becomes:

$$G = \left[52,190 - 8,802 \left(\rho_{15}{}^2 \times 10^{-6} \right) \right] \times \left[1 - 0,01(w + a + s) \right] + 0,094\ 2s$$

6.2.1 A simplified form of this equation gives results sufficiently accurate for practical purposes, where water content and ash content are within normal levels [0,3 %(*m/m*) and 0,05 %(*m/m*) maximum respectively], and this is:

$$G = 61,0 - 17,6 \left(\rho_{15} \times 10^{-3} \right) - 0,34s$$

6.3 The equation for net specific energy, N_a, in megajoules per kilogram, is that proposed by Cragoe (with conversions), and is:

$$N_a = \left\{ 46,704 - \left[8,802 \left(\rho_{15}{}^2 \times 10^{-6} \right) \right] + \left[3,167 \left(\rho_{15} \times 10^{-3} \right) \right] \right\} \times \left[1 - 0,01(w + a + s) \right] + 0,094\ 2s - 0,024w$$

6.3.1 A simplified form of this equation is also accurate enough for practical purposes under the same conditions as 6.2.1, and is:

$$N_a = 55,5 - 14,4 \left(\rho_{15} \times 10^{-3} \right) - 0,32s$$

6.4 Tables for Q_s versus ρ_{15} is a useful adjunct to the equation for gross specific energy, and simplifies calculations considerably, and a similar adjunct could be prepared for the term between the corrugated parentheses in the equation for net specific energy. Tables to include sulfur content are possible [to cover density values of 950 kg/m^3 to 1 009 kg/m^3, and sulfur contents from 0,5 %(*m/m*) to 4,0 %(*m/m*), illustrates some 2 100 values], but show no advantage over the simplified equations, and do not make any adjustment for water content and/or ash content. Similarly, charts, widely used, have the same limitations as tables in that they can only illustrate density and sulfur contents, and are likely to introduce interpolation errors which are not insignificant. Unless accurate calculations are required, the use of the simplified equations is preferred to charts and tables.

Annex A
(informative)

Raw data for specific energy calculations

A.1 Origin of data

The data given in Table A.1 has been transcribed from the original handwritten sheets included as an annex to the French experts report of December 1981. The data has been tidied up in terms of consistency of reporting sensitivity, and the densities have been reported here in terms of kg/m³ instead of the kg/l originally used. The order of the data has been changed to give a more logical progression, and particularly, to place the specific energy data together.

The specific energy data is reported as 'measured (M)' followed by 'calculated (C)', where the calculation is carried out by the **original** Cragoe equation. The difference (M – C) is thus generally positive, showing the normal underestimate (see 4.1.3). Where the difference is negative (M < C), the figure is shown in parentheses.

Table A.1 — Raw data for the calculation of specific energy

No.	ρ_{15} kg/m³	s %(m/m)	w %(m/m)	a %(m/m)	Carbon %(m/m)	Hydrogen %(m/m)		Gross specific energy MJ/kg		
						Meas.	Calc.	Meas.	Calc.	M – C
1	958	1,57	<0,05	0,035	85,81	11,24	11,39	43,45	43,11	0,34
2	993	3,78	0,3	0,045	84,87	10,31	10,63	41,33	41,80	0,13
3	929	0.36	0,3	0,025	86,37	12,05	12,00	44,35	44,04	0,31
4	941	0,89	<0,05	0,010	86,65	11,81	11,77	44,12	43,78	0,34
5	953	2,05	0,05	0,025	86,01	11,55	11,47	43,58	43,17	0,31
6	992	3,80	<0,05	0,035	84,99	10,46	10,70	42,16	41,92	0,24
7	984	3,22	<0,05	0,015	85,19	10,71	10,88	42,61	42,26	0,35
8	935	0,93	<0,05	0,020	86,07	12,03	11,86	44,48	43,86	0,62
9	931	1,26	<0,05	0,020	85,71	12,06	11,89	44,40	43,81	0,59
10	956	2,68	<0,05	0,020	84,85	11,50	11,34	43,50	42,91	0,59
11	948	3,31	<0,05	0,020	84,16	11,56	11,39	43,35	42,82	0,53
12	934	0,36	<0,05	0,020	86,61	12,06	11,93	44,88	44,07	0,81
13	990	4,00	<0,1	—	85,40	10,40	10,70	42,29	41,88	0,41
14	965	3,45	<0,1	0,027	84,45	10,85	11,13	43,07	42,47	0,60
15	993	3,80	<0,1	0,020	84,40	9,80	10,70	42,13	41,89	0,24
16	979	3,90	<0,1	0,070	84,60	10,40	10,90	42,13	42,07	0,06
17	976	3,75	—	0,040	85,30	10,90	10,90	42,13	42,23	(0,10)
18	978	3,90	<0,1	0,030	84,80	10,30	10,90	42,54	42,10	0,44
19	971	3,50	0,2	0,020	84,70	11,10	11,20	42,59	42,32	0,27
20	989	3,90	0,1	—	85,30	10,65	10,74	42,17	41,93	0,24