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HYDROCARBON FUELS

Production, Properties and Performance of Liquids and Gases

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To
KATHLEEN R.

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Preface

Since the discovery of crude petroleum in commercial quantities just over a century ago, the production of hydrocarbon-type fuels has been showing a healthy growth rate both in absolute terms and as a proportion of the overall energy market. Factors contributing to these developments include the comparative ease of winning and handling materials in the liquid phase, the high stored energy density, the relative freedom from ash and major contaminants, the flexibility of control in combustion, and the capability of conversion into many fuel types of widely differing properties.

Until a few years ago it was possible to predict with some confidence a steady climb in the global consumption of energy, with a growing proportion provided by hydrocarbon fuels in liquid and gaseous forms. However, the energy world has now been faced with three crucial problems. The first is posed by the imbalance of energy usage, with one half of the world's population taking about 90 per cent of the commercial energy consumption. The second concerns the damage being done to the environment by the uncontrolled emission of harmful products resulting from energy conversion, and this has stimulated development of more economic and closely controlled systems of combustion. Rising prices and politically imposed shortages have highlighted the third, most profound, problem of the finite nature of fossil-type fuels, and have led to even further efforts for economy, and vigorous exploration for both additional and alternative supplies of energy. Sometimes the solutions to these problems appear to be in parallel, and at other times in conflict.

In an ideal world structure, these problems would be tackled by some world government body, which would redistribute the energy wealth more equitably, and co-ordinate the search for unlimited supplies of inexpensive energy that could be used without risk to environmental health. In the real world, this target might be approached nationally by far-sighted integration of energy consumption, and active research into all aspects of energy usage and forecasting, particularly by the technically developed nations. This would replace such present anomalies as individual energy industries competing for customers and undertaking localised research in an unco-ordinated way, with

logical steps to integration blocked by taxation and various political restrictions.

Paradoxically the ultimate target would appear to be the abandonment, as fuels, of all fossil products, including the hydrocarbons, so that they are available solely as chemical feedstock for industrial, constructional, medical and domestic materials, many of which might be recycled over and over again. This would entail the successful and extensive development of nuclear power plant, including the control of fusion, and the reliance on continuous sources of energy income which do not disturb the thermal equilibrium of this planet. Until this ideal situation is approximated to, the world must continue to rely on its dwindling stock of fossil-energy capital and, since it *is* dwindling, learn to husband this resource with increasing skill and responsibility. Since hydrocarbons form a very substantial part of this precious commodity, a broad but concise appraisal of the nature, properties and applicational performance of these fuels appears to be warranted. Hence this present work.

Most commercial fuels comprise various blends of hydrocarbon materials, and this book covers all petroleum fuels of commercial interest ranging from natural gas (methane) to the heavy residual fuel oils, together with fuel materials derived from alternative sources. Since the aviation fuels, by their very nature, demand the highest quality and precision in their specification, they lend themselves particularly well to exemplify the influence of component content on performance. Their relative importance with regard to *quantity* of production is, however, quite low.

In any complex subject, a real depth of understanding requires a knowledge of the underlying fundamental components and/or processes. With fuel technology, these fundamentals comprise the structure and properties of the fuel molecules themselves, and of their constituent atoms. Properties and reactions of fuel in bulk can then be seen properly as aggregates of the individual properties and reactions of these basic building units. A strong thread of fuel chemistry and physics therefore runs through this book, ranging from the component parts of the hydrogen and carbon atoms, through the refining, testing and handling of finished hydrocarbon products, to their subsequent combustion and emission.

The book opens with a broad picture of the world energy scene, and of the place of hydrocarbon fuels within it. The problems and techniques associated with the detection and winning of the main source, crude oil, are covered briefly.

Section II of the book presents first a summary of the main features of the structure of atoms and molecules, and the nature of their bonding forces. (Background details of these fundamentals are reviewed in appendix 1, and are necessary for a full understanding of the spatial structure of hydrocarbon molecules, and the non-rotation of multi-carbon bonds.) Chapter 2 continues with a simple chemical picture of hydrocarbon-type molecules, and begins to show how molecular structure influences their physical behaviour, that is,

how chemistry helps to explain, and even to predict, fuel performance in engineering practice. Chapter 3 shows how heat quantities can be accounted for by means of a simple system of thermal book-keeping, whereas chapter 4 indicates that the additional knowledge of reaction rates permits the calculation of such performance parameters as the proportions of products resulting from combustion, and the level of temperature reached. Chapter 5 covers some of the more important physical properties of fuels in bulk, outlining the laboratory-bench tests available, and giving typical results. The inter-relationship of such properties is stressed, and a concise view of property variation with fuel type is presented by plotting these results using relative density as a basis of comparison. Information on additional physical, and some chemical, tests is given in chapter 6.

Section III of the book covers the practical applications of commercial hydrocarbon fuels, and commences with fuel-refining processes, and a broad description of the main fuel types and their uses. The various problems of handling fuels are outlined in chapter 8. Chapters 9 and 10 cover briefly the major aspects of fuel performance in piston engines and continuous combustors, respectively, and chapter 11 summarises the emissions problems arising from hydrocarbon fuel combustion. The final chapter presents a brief review of possible alternative fuels, and of the various methods under active consideration for the more efficient conversion of energy from fuel-borne chemical to the widely useful electrical form. Details of representative hydrocarbon properties, and of typical commercial fuel specifications, are given in appendixes 2 and 3.

The book is intended for students and practising engineers concerned with the utilisation of hydrocarbon fuels. It contains material suited to courses leading to Higher National Certificates and Diplomas, Institute of Fuel Diplomas in Fuel Technology, the relevant CEI Part II examinations, and to first and higher degrees in departments of fuel technology, and of aeronautical, agricultural, automobile, chemical, marine and mechanical engineering in engineering colleges, polytechnics and universities.

Acknowledgement is made gratefully to colleagues and students of the University of Newcastle, N.S.W., and the Cranfield Institute of Technology, Bedfordshire, for much valued assistance in the form of discussion, feedback and joint research effort, and particularly to Professor A. H. Lefebvre, Head of the School of Mechanical Engineering at Cranfield, for the facilities which made this work possible, and for approval to use Cranfield material. Permission to reproduce published data has been kindly provided by the Associated Octel Company Limited, the British Standards Institution, and the IPC Science and Technology Press Limited. The ready assistance provided by the energy industry over the years is also very much appreciated, together with valuable guidance offered by the Macmillan Press.

Units

In any system of units, a number of quantities are defined as basic to the system, and all the remaining quantities are derived from them. If the system is coherent, the products and quotients of any two or more unit quantities themselves become the units of the derived quantities. Hence, in an expression such as Newton's second law, given by

$$F \propto ma$$
$$= kma$$

the numerical value of the constant k is unity in a coherent system, but has some other value in a non-coherent system.

The confusion arising from alternative systems of units having different values of k , and from the use of a common term (pound) with different meanings, has been eliminated by the adoption of a rationalised system of metric units known as SI (Système International d'Unités). This system is coherent, and adopts a derived unit that is common to the mechanical, electrical and most other forms of energy. SI defines the following seven base units.

length	metre (m)
mass	kilogram (kg)
time	second (s)
electric current	ampere (A)
thermodynamic temperature	kelvin (K)
luminous intensity	candela (cd)
amount of substance	mole (mol)

Notes

- (1) The kelvin is also used for temperature intervals.
- (2) The mole relates to what was formerly called the 'gram-mole', and not to the 'kilogram mole (kmol)'

SI includes the following derived units.

force	newton (N) = kg m/s ²
pressure	pascal (Pa) = N/m ²

energy	joule (J) = N m
power	watt (W) = J/s

No change is made to any symbol to indicate the plural.

A table of units based on the SI has been recommended by the Institute of Petroleum, London (*Recommended SI Units*, 1970) for use in the oil industry. This includes some earlier metric units, such as the litre and the bar, which are not part of the SI but are considered acceptable. These recommended units have been adopted throughout this book, and any quantities specified in other units are presented as such, followed by the recommended equivalent in parenthesis. Since the universal adoption of these recommended units is as yet incomplete, the following conversion factors are given.

length	1 ft = 0.3048 m 1 mile = 1.6093 km
volume	1 U.K. gal = 1.201 U.S. gal = 4.546 litres 1 U.S. gal = 0.8327 U.K. gal = 3.785 litres 1 U.S. barrel = 34.972 U.K. gal = 42 U.S. gal = 158.9 litres
mass	1 lb = 0.4536 kg
density	1 lb/ft ³ = 16.0185 kg/m ³
force	1 lbf = 4.4482 N
pressure	1 lbf/in ² = 6.894 76 kPa 1 mm Hg = 133.322 Pa 1 atm = 101.325 kPa
energy	1 B.t.u. = 1.0551 kJ 1 kcal = 4.1868 kJ 1 kWh = 3.6 MJ 1 h.p. h = 2.6845 MJ
specific energy	1 B.t.u./lb = 2.326 kJ/kg
specific energy	1 B.t.u./lb °R = 1 CHU/lb K = 4.1868 kJ/kg K
capacity	
volumetric energy	1 B.t.u./ft ³ = 0.0373 kJ/1 (or MJ/m ³) 1 B.t.u./U.K. gal = 0.232 kJ/1 1 B.t.u./U.S. gal = 0.278 kJ/1
power	1 h.p. = 745.7 W 10 ⁹ h.p. h/a = 85.125 MW 10 ⁹ B.t.u./a = 0.033 46 MW 1 MJ/a = 31.71 kW

Representative interconversions between volume, mass, weight and energy are shown in table U1 for crude oil, based on world average density and calorific value. Table U2 shows the energy equivalents of quantities of different fossil fuels.

Table U1 *Approximate conversion factors for crude oil* (based on world average density and calorific values; derived from data published by the British Petroleum Co. Ltd, and by Shell International Petroleum Co. Ltd)

	Volume (barrel)	(long ton)	(tonne (t))	Mass or Weight (short ton)	(kN)	(kg)	(lb)	Energy (MJ)
1 barrel	1	0.134	0.136	0.150	1.338	136.4	300.8	6 089
1 long ton	7.45	1	1.016	1.120	9.964	1016.3	2240	45 360
1 tonne (t)	7.33	0.984	1	1.102	9.804	1000	2204.6	44 633
1 short ton	6.65	0.893	0.907	1	8.898	907.6	2000	40 507
1 kN	0.7477	0.1004	0.1020	0.1124	1	102.0	227.3	4 553
1 kg	0.00733	0.98×10^{-3}	0.0010	0.0011	0.0098	1	2.2046	44.63
1 lb	0.00332	0.45×10^{-3}	0.45×10^{-3}	0.0005	0.0044	0.4536	1	20.25
1 MJ	0.1642×10^{-3}	0.0220×10^{-3}	0.0224×10^{-3}	0.0247×10^{-3}	0.2196×10^{-3}	0.0224	0.0494	1

1 barrel/d = 365 bbl/a = 49.8 t/a = 70.6 kW

Derived from data published by The British Petroleum Co. Ltd, and by Shell International Petroleum Co. Ltd.

Table U2 Fuel energy equivalents (derived from data published by the Shell International Petroleum Co. Ltd)

	b.o.e.	t.c.e.	t.o.e.	m.c.f.n.g.e.
1 barrel oil equivalent (b.o.e.)	1	0.211	0.136	0.006
1 tonne coal equivalent (t.c.e.)	4.73	1	0.645	0.027
1 tonne oil equivalent (t.o.e.)	7.33	1.550	1	0.043
1 million ft ³ natural gas equivalent (m.c.f.n.g.e.)	172	36.4	23.5	1

10^9 b.o.e. = $6\,089 \times 10^9$ MJ

10^9 b.o.e./a = 0.1931×10^6 MW

10^9 t.c.e. = 0.02884×10^{15} MJ

10^9 t.c.e./a = 0.9144×10^6 MW

10^9 t.o.e. = 0.04463×10^{15} MJ

10^9 t.o.e./a = 1.4153×10^6 MW

10^9 m.c.f.n.g.e. = 1.0489×10^{15} MJ

10^9 m.c.f.n.g.e./a = 33.2596×10^6 MW

Notes: 1. The following symbols are used for time periods: second (s), minute (min), hour (h), day (d), year (a).

2. bbl = US barrels.

Notation

When two symbols are given for one item, upper case represents an extensive property (dependent on mass), and lower case a specific property (per unit mass). When one symbol is used for more than one item, the particular meaning in any instance is apparent from the context.

<i>A</i>	air mass or volume
(D)	dissociated
<i>d</i>	diameter of particle
<i>d</i>	relative density at 60/60 °F
E.A.D.	equilibrium air distillation
<i>F</i>	force
<i>F</i>	fuel mass
f.b.p.	final boiling point
<i>G, g</i>	Gibbs free energy function
(g)	gas
(gr)	graphite
<i>H, h</i>	enthalpy
<i>I</i>	specific impulse
i.b.p.	initial boiling point
i.m.e.p.	indicated mean effective pressure
<i>K</i>	equilibrium constant
<i>k</i>	rate constant
<i>L</i>	liquid mass or volume
LN	luminometer number
(l)	liquid
<i>M</i>	relative molecular mass (formerly molecular weight)
MON	motor method octane number
<i>m</i>	mass
<i>m</i>	number of moles of oxygen
<i>N</i>	rotational speed in revolutions per minute
(N-D)	non-dissociated
<i>n</i>	number of moles (usually of combustion products)
<i>P</i>	pressure

Q, q	heat transfer
R	gas constant
R_0	universal gas constant
RON	research method octane number
r	ratio
S, s	entropy
s.f.c.	specific fuel consumption
(s)	solid
S.V.I.	smoke volatility index
T	absolute thermodynamic temperature (K)
T.E.L.	tetraethyllead
T.M.L.	tetramethyllead
T.V.O.	tractor vaporising-oil
t	empirical temperature ($^{\circ}\text{C}$ or $^{\circ}\text{F}$)
t.d.c.	top dead centre
U, u	internal energy
V, v	volume
V	vapour mass or volume
v	velocity
W, w	work transfer
W.I.	Wobbe index
α	cut-off ratio in diesel cycle
γ	ratio of specific heat capacities
η	dynamic viscosity
ν	kinematic viscosity
σ	fuel density
ρ	density
ϕ	equivalence ratio

Superscripts

$^{\circ}$	standard state of 25°C and 1 atm
'	concentration basis

Subscripts

a	atomisation
atm	atmospheric pressure
E	equilibrium
E	exhaust
F	forward
f	formation
f	fuel vapour
f	fundamental
I	initial
I	inlet
i	any arbitrary reactant component

<i>j</i>	any arbitrary product component
obs	observed
<i>P</i>	pressure
R	reverse
res	resonance
r	reaction
s	stoichiometric
sp	specific
sp	spontaneous
<i>T</i>	temperature
T	total
<i>v</i>	volume
<i>v</i>	vaporisation
WG	water gas