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METROLOGY FOR THE THERMODYNAMIC CHARACTERIZATION OF BIOFUELS

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Abstract − The most important physical parameter of any fuel is its energy content which is usually described by its specific inferior calorific value. The inferior calorific values of two biodiesels, rape seed methyl ester (RME) and soy bean methyl ester (SME) have been determined by precision bomb calorimetry to 37088.9 ± 11.0 Jg^{-1} and 36998.7 ± 8.2 Jg^{-1}, resp.

Keywords Biofuel, combustion calorimetry, thermodynamics.

1. INTRODUCTION

Biofuels are attractive renewable energy carriers esp. for mobile applications where they replace petrol (as ethanol) and diesel (as biodiesel, i. e. methyl esters of fatty acids from oil seeds). Ethanol, as a pure chemical, has distinct physical and chemical properties which are only modified by impurities. These impurities usually do not affect the energetic properties of the fuel. On the other side, biodiesel consists of different chemical species which are unstable under usual storage conditions. The compositions of biodiesels depend on the raw materials used, their storage conditions, contents of impurities and use of stabilizers.

The energy content of a certain amount of biofuel, expressed as its inferior calorific value H_i, is one of the most important quantity for characterizing the commercial value of the fuel. It is used, for example, for the determination of the efficiency of biofuel fueled processes, the greenhouse gas emission factor, or the admixture of biofuel to fossil fuel. In future, the energy content of the fuel together with its CO_2 production will be the basis for taxation [1].

Published values for the calorific values of biodiesels are scarce and differ. Uncertainties are generally not given, only rarely the exact chemical composition of the biofuel has been given. Traceability to the SI is never possible. As an unfortunate consequence, the data used in relevant documents, e. g. EC directives, are only rough estimates of the true values and just valid for an average biofuel [2].

It is the aim of the current investigations to develop a methodology for the determination of thermodynamic parameters of biofuels, in particular biodiesels, with proven traceability to the SI. These thermodynamic parameters comprise calorific value (inferior and superior), enthalpy of vaporization, enthalpy of crystallization, standard enthalpy of formation. Because of the great variety of the methyl esters comprising biodiesel, only selected substances will be investigated experimentally. These data will serve as the basis for the development of quantum mechanical computation and semi empiric calculation methods to estimate the properties of those materials which are experimentally inaccessible due to physical constraints or lack of material. In this paper, first results on the experimental determination of calorific values by calorimetry are described.

2. EXPERIMENTAL

Combustion calorimetry has been performed by employing two different isoperibolic bomb calorimeters of conventional design, one home-made the other one commercially. The results of the calorimeters do not differ significantly. Calibration of the calorimeters was performed with benzoic acid (certified by NIST, USA for enthalpy of combustion, designated SRM 39j).

Preliminary experiments have been performed on model substances for biodiesel, namely 1,2,3-propanetriol triacetate, 1,2-ethanediol diacetate, and 1,2-ethanediol monoacetate to prove the applicability of the tools [3].

The materials investigated here were rape seed methyl ester (RME) and soy bean methyl ester (SME) which have been received from ADM Hamburg AG, Hamburg, Germany. Their fatty acid profiles are given in table 1.

TABLE 1. Fatty acid profile of RME and SME

	RME	SME
Fatty acid [*]	c / mg g^{-1}	c / mg g^{-1}
C14:0	0.507	0.90
C16:0	46.0	107
C18:0	16.5	40.1
Σ C18:1 isomers	601	249
Σ C18:2 isomers	197	497
Σ C18:3 isomers	87	73
C20:0	5.61	4.1
C10:0	0.089	
C12:0	0.155	0.152
C15:0	0.224	0.174
C16:1	2.077	0.869
C17:0	0.554	0.953
C20:1	13.065	2.460
C20:2	0.711	0.381

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TABLE 1. Fatty acid profile of RME and SME (contd.)

	RME	SME
Fatty acid *	c / mg g^{-1}	c / mg g^{-1}
C20:3n3	0.119	
C22:0	3.214	4.565
C22:1n9	4.176	0.227
C22:2	0.159	
C23:0	0.2267	0.56
C24:0	1.205	1.554
C24:1	1.487	0.307
Sum of unknown	18.9	16.7

* The first number indicates the number of carbon atoms in the fatty acid chain and the second number is the number of double bonds. n3 and n9, resp., indicate the position of the double bond counting from the end of the fatty acid chain. The following picture shows the system of numbering [4].
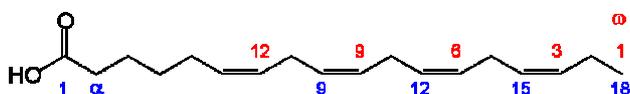
3. RESULTS

The calorific values determined for RME and SME are given in Table 2 and compared with literature values.

TABLE 2. Inferior calorific values of RME and SME

	Diesel	RME	SME
	H_i / J g^{-1}	H_i / J g^{-1}	H_i / J g^{-1}
this work *	42450.7 ± 7.5	37088.9 ± 11.0	36998.7 ± 8.2
Wörgetter [5]	43070	37160	37140
Knothe [6]		37300	37372 37388
EC [2]	43000	37000	37000

* Given is also the standard deviation of the mean.

4. CONCLUSION

It is obvious from the results that the data currently used by the EC do not reflect the variability of the biodiesels. As a consequence, citizens of the EU are charged taxes, pay for greenhouse gas emissions or receive subsidies mostly either too much or too little but rarely the correct amount.

Further research is necessary to determine the thermodynamic values of a larger number of biodiesels from different sources. In case the variability of the data exceeds the level acceptable to society, instruments, methodologies and standards allowing a simple, quick and reliable determination of the calorific value on site have to be developed.

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