
TECHNICAL NOTE

RENEWABLE ENERGY CONTENT OF FATTY ACID METHYL ESTERS (FAME) AND GLYCEROL

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1. Introduction

In recent years, there have been many reasons that have encouraged the European Parliament to endorse support actions and incentives for the development of renewable Energy [Parish 2006]. Electricity production and transport are among the most interesting sectors affected by Directives 2001/77/EC and 2003/30/EC as well as the additional 2003/96/CE which applies to both sectors. One of the products, particularly affected by these actions, is FAME, known as biodiesel. Its characteristics are specified in two provisions that have been active since 2003 in Europe and since 2004 in Italy: the UNI EN 14213 – “Heating fuels. Requirements and test methods” and the UNI EN 14214 – “Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods”.

Taking into account biofuel, FAME is the only product produced by a chemical process based on the reaction between the glycerides present in vegetable oil and a product from a fossil source: methanol. Besides FAME, which is made up of a mixture of methyl esters (ME), the process generates a reaction by-product, glycerol (GL), which is also used as a bio-fuel. Both the molecules produced contain atoms from the methanol within the reagent and, therefore, are not considered renewable. Given that they are energy products produced from a reaction between a renewable material and a fossil source, it is necessary to define the renewable energy they contain, for instance, this is necessary when applying the biomass incentives according to the European provisions and for testing the biofuels and the bioliquids required by the new Directive 2009/28/CE (RED). In this manner, the

latter will therefore provide a methodological and practical contribution. Generally, the heat produced by a reaction (combustion is a reaction) can be estimated through experiments (calorimeter) or, indirectly, by calculating the reaction enthalpies. The overall energy developed from a complete molecule combustion can be measured experimentally with the calorimetric method. Nevertheless, this method does not indicate the extent to which each molecule part contributes to the heat produced. The indirect methods involve calculation procedures, which are based on precise information about the reaction and the thermochemical data of the molecules or the parts involved.

One of the most diffused indirect methods is based on the knowledge about the enthalpy formation of the reagents and the products involved in the reaction [Chambers 1975, Lanfred 2001]. In any case, in the absence of data about complex molecules various strategies are used to calculate the reaction enthalpy of a chemical process using the Benson group additive method [Nomen 2005]. This method is based on the precise knowledge of the molecular structures involved in the reaction and the identification of the group of atoms consists of at least two chemical bonds [Chopey 2004]. Besides being an easily applicable approach, it can usually predict thermochemical data with the same uncertainty of experiments [Aa.Vv. 2004]. Nevertheless, neither calculation modality allows the estimation of the energy contributed by the single atom. There is also another method based on the knowledge of the reagent and the product molecular structure and bond enthalpy (ΔH_b) or of bond dissociation energies which is very immediate. The ΔH_b is a positive number corresponding to the energy required to break the molecule into its fragments, or the energy released when the bond is formed [Salmon 2006]. All materials are made of atoms which are tightly bonded to each other to form molecules of the materials. When a chemical reaction occurs, the materials change into other materials through bond breakage and new bond formation [Kubota 2002]. Any chemical reaction, including combustion, starts with a first phase of bond breaking within the reagent molecule, which requires the ab-

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sorption of the heat system ΔH_{br} , concluding with a second phase of new bond formation of products in which ΔH_{bp} heat develops. The energetic balance of both enthalpies determines the heat of the ΔH_r reaction (1). In particular:

$$\Delta H_r = \Delta H_{bp} - \Delta H_{br} \quad (1)$$

When the ΔH_r of the reaction is negative, the reaction is exothermic, as in the case of combustion.

The ΔH_b depends on the type and the energetic state of the atoms based on the electron of each atom. Although the exact energetic state of the materials should be evaluated by quantum mechanics, an overall energetic state is evaluated by the ΔH_b determined experimentally. The total chemical bond energy of the molecule atoms is equal to the energy of the molecule [Kubota 2002].

Considering the aspects mentioned in the introduction and according to the analysis regarding the energy aspects of the chemical reactions, it was considered interesting to develop a method for calculating the content of the renewable energy fraction in GL and FAME products using the traditional process based on the transesterification reaction. In other words, the degree of renewability of the chemically modified generated biomass products can be calculated using this method. At the same time the amount of energy produced from their combustion and which can be attributed to the initial biogenic matter can also be estimated. A calculation criteria, backed with simplified analytic measurements, is especially used for the FAME products. This method might be useful in understanding the various energy contents in other similar renewable energy products. Besides FAME, there are other synthesis products derived from renewable and non-renewable materials. An example of this is the Ethyl Tertiary Butyl Ether (ETBE). On the contrary, the production of ethyl esters from renewable ethanol ensures the renewability of the products. Nevertheless, there is still no comparative criterion for product renewability. The aim of this study is to fill up this gap.

2. Material and methods

This study was developed and presented in two distinct parts: the calculation methodology to estimate the renewable energy content in FAME and GL and the development of an applied analysis method for FAME.

2.1 Remarks on transesterification reactions

This equation is for a simplified form of a transesterification reaction (*figure 1*) where R_1 , R_2 , and R_3 are long chains of carbons and hydrogen atoms, called the fatty acid chain. Two of the most commonly used

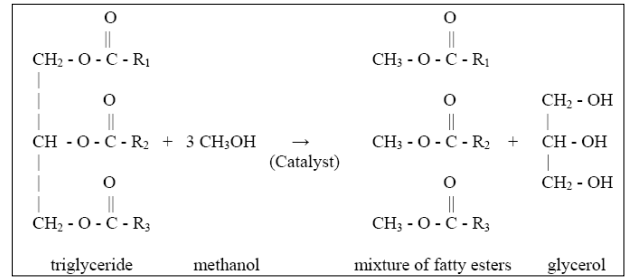


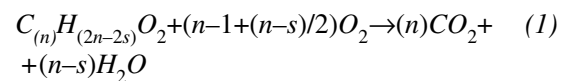
Fig. 1 - Transesterification reaction chart (processed by Van Gerpen).

catalysts for transesterification are NaOH and KOH. The reaction mechanisms can vary according to the conditions of the reaction [Van Jerpen 2004].

Nevertheless, it is possible to identify the methanol molecule in the reaction products through a mechanism of mass balancing in the simplified reaction, i.e., the methoxide added to the carboxyl of the ME and the hydrogen in the functional group $-OH$ of the GL. Analyzing the chemical bonds in the ME it is possible to consider the derivatives from the methanol 3 C-H bonds and the C-O 1.5 bonds as well as half the O-H bond in GL. This analysis is fundamental to establish which bonds contribute to identify the non-renewable and renewable energetic fraction of the produced ΔH_r .

2.2 Analysis of the combustion reaction and the calculation of the non-renewable energetic fraction

The complete combustion of ME and GL is defined by the generic reactions (I and II), respectively:



in which n is the number of carbon atoms of ME and s is the number of unsaturations present. Given the structure of the molecule and in function of n and s , it is possible to calculate the total number of the various chemical bonds forming the reagent molecules and the reaction products. Only three elements are involved in the structure of the molecule: carbon, hydrogen and oxygen. As regards to the reagents, on the one hand these elements are found in the bonds C-C and C-H, forming a carbonaceous chain and the methyl of the methoxide group in the ME and the entire carbonaceous structure of the GL; on the other hand, the bonds C=O and C-O form the carboxyl group of the fatty acids and the bond O=O forms the oxygen. Within the reaction products, combustion water and carbon dioxide, the bonds are represented by O-H and C=O. Some of these bonds are hybrids, that is, consisting of an atom that is originally present in the triglyceride and another atom originally present in methanol. The value of ΔH_b has been defined for

every bond, based on literature, with reference to the molecules or functional groups that most resemble the ones at issue in this study. Moreover, the member molecule in the combustion reaction and the number of bonds formed from a generic ME (table 1) and GL (table 2) were indicated together with other data.

2.3 Reaction energy calculation

From (1) it is possible to determine the general calculation equations for combustion ΔH_r for every product considered. In the case of ME and GL, the calculation of ΔH_r is described in table 3.

Theoretically, the value of ΔH_r coincides with the high calorific value of the product. The energetic ΔH_i value is determined by subtracting the enthalpy of water evaporation generated in combustion ($H_E = 40.7$ kJ/mol), theoretically expressing the low calorific value. In particular:

$$\Delta H_{i(ME)} = \Delta H_{r(ME)} - (n-s) \times H_E \quad (4)$$

$$\Delta H_{i(GL)} = \Delta H_{r(GL)} - 4 \times H_E \quad (5)$$

The same calculation criteria, described above for the atoms at issue, can be used to calculate the en-

Bond	Bibliographic reference	ΔH_b (kJ/mole)	Affected molecule	Bond (n)
C-H	(Lide 1999) – Propane	423	ME	2n-2s
C-C	(Kubota 2002), (Lide 1999), (Silvestroni 1984) – Average value	367	ME	n-s-2
C=O _(I)	(Kubota 2002) – Ketone	766	ME	1
C-O	(Kubota 2002) – Generic	350	ME	2
C=C	(Kubota 2002) – Generic	599	ME	S
O=O	(Kubota 2002) – Oxygen	498	O ₂	n-1+(n-s)/2
C=O _(II)	(Hueey 1983) – Carbon dioxide	803	CO ₂	2n
O-H _(I)	(Lide 1999) – Water	497	Water	2(n-s)

TABLE 1 - Enthalpic characteristics and the main data on chemical bonds in ME combustion.

Bond	Bibliographic reference	ΔH_b (kJ/mole)	Affected molecule	Bond (n)
C-H	(Lide 1999) – Propane	423	GL	5
C-C	(Kubota 2002), (Lide 1999), (Silvestroni 1984) – Average value	367	GL	2
C-O	(Kubota 2002) – Generic	350	GL	3
O-H _(II)	(Lide 1999) – Ethanol	438	GL	3
O=O	(Silvestroni 1984) – Oxygen	498	O ₂	3.5
C=O _(II)	(Hueey 1983) – Carbon dioxide	803	CO ₂	6
O-H _(I)	(Lide 1999) – Water	497	Water	8

TABLE 2 - Enthalpic characteristics and the main data on chemical bonds in GL combustion.

Product	Calculation of ΔH_r
Methyl ester	$\Delta H_{r(ME)} = (2n _ \Delta H_{C=O(II)} + 2(n-s) _ \Delta H_{O-H(I)}) - ((2n-2s) _ \Delta H_{C-H} + (n-s-2) _ \Delta H_{C-C} + \Delta H_{C=O(I)} + 2 _ \Delta H_{C-O} + s _ \Delta H_{C=C} + (n-1+(n-s)/2) _ \Delta H_{O=O}) \quad (2)$
Glycerol	$\Delta H_{r(GL)} = (6 _ \Delta H_{C=O(II)} + 8 _ \Delta H_{O-H(I)}) - (5 _ \Delta H_{C-H} + 2 _ \Delta H_{C-C} + 3 _ \Delta H_{C-O} + 3 _ \Delta H_{O-H(II)} + 3.5 _ \Delta H_{O=O}) \quad (3)$

TABLE 3 - Calculation of ΔH_r for ME and GL.

thalpy from the non-renewable part of the molecule (ΔH_{NR}). The following equations were used:

$$\Delta H_{rNR(ME)} = (1.5 \times \Delta H_{C-O(II)} + 1.5 \times \Delta H_{O-H(I)}) - (6) \\ (3 \times \Delta H_{C-H} + 1.5 \times \Delta H_{C-O})$$

$$\Delta H_{rNR(GL)} = (1.5 \times \Delta H_{O-H(I)}) - (1.5 \times \Delta H_{O-H(II)}) \quad (7)$$

$$\Delta H_{iNR(ME)} = \Delta H_{rNR(ME)} - 1.5 \times H_E \quad (8)$$

$$\Delta H_{iNR(GL)} = \Delta H_{rNR(GL)} - 1.5 \times H_E \quad (9)$$

The fraction of non-renewable energy of the molecule (E_{NR}) is obtained from the ratio of ΔH_{iNR} and ΔH_i

$$E_{NR(FAME)} = \Delta H_{iNR(ME)} / \Delta H_{i(FAME)} \times 100 \quad (10)$$

$$E_{NR(GL)} = \Delta H_{iNR(GL)} / \Delta H_{i(GL)} \times 100 \quad (11)$$

In order to evaluate the approximation level of the calculation method used, it was considered necessary to compare the calculated ΔH_r values for every FAME with the respective values obtained through experiments (ΔH_c). The latter are average values deduced from the database of the National Institute of Standard Technology (NIST). For every ME, the absolute error and the percentage error (ΔE) were calculated with reference to the ΔH_r data obtained through experiments. The estimations were carried out on the ME that mostly represented the corresponding fatty acids of the most common vegetable oils. Considering that FAME is made up of variable mixtures of ME, an average value, which takes into consideration the percentage composition of the ME (C_{ME}) and the respective E_{NR} values, must be used to calculate the non-renewable part of the entire EF_{NR} produced. In the case of a generic FAME, the value of EF_{NR} is calculated as follows:

$$EF_{NR} = \sum (E_{NR(ME)_x} \times C_{ME_x}) / 100 \quad (12)$$

in which x indicates the generic ME present in FAME.

2.4 Experimental methods to measure the non-renewable fraction of FAME

The proposed calculation method was applied to some products to verify its feasibility. For this purpose, 15 vegetable oil samples were picked from most representative especially in terms of variability in the length of glyceride acid chains. The size of the molecule from fatty acid plays an important role on the fraction of renewability of each ME. Gas-chromatographic analyses were carried out to determine the C_{ME} and to estimate the amount of saponification (N_S).

The number of average carbon atoms (N_{CM}) of FAME was calculated as follows, taking into consideration the acidic composition and the function of (13):

$$N_{CM} = \sum (N_{C(ME)_x} \times C_{ME_x}) / 100 \quad (13)$$

in which N_C is the number of carbon atoms in each ME. The value of N_C expresses the average molecule mass of glyceride contents in vegetable oil to be compared with the corresponding FAME. Specifically, each of them was tested for the correlation between EF_{NR} and the N_C value. Subsequently, the correlations between the value of N_C and that of N_S and, finally, between the EF_{NR} values and those of N_S were verified.

3. Results

Table 4 shows a series of specific results regarding each ME. The data of the ΔH_r calculated with the proposed methodology and the ΔH_c taken from the NIST database are also shown in the table. It has been observed that the ΔE values are rather contained and consolidated around an average of 0.6% (corresponding to about 65 kJ/mol) with a maximum of -2.5%. For the purpose of this study, these results are encouraging and favourably support the proposed calculation method. The E_{NR} values of each ME are also reported in the table. It can be observed that since the amount of energy coming from the non-renewable part of the molecule (methoxide) is constant, the E_{NR} value is strongly dependent on the length of the ME. In unsaturated molecules, the values vary between 2.4% of ME with 7 carbon atoms and 0.7% of ME with 23 carbon atoms.

Similarly, table 5 shows the same results obtained for GL. It has been noticed that the ΔE is higher compared to the calculations carried out on the ME and a little less than 10% lower. Although the non-renewable part, i.e. hydrogen derived from methanol, always forms a bond -OH before and after the reaction, the calculated E_{NR} is still equal to 1.6%, taking into consideration that the -OH bond before and after the reaction has various chemical characteristics and, therefore, different ΔH_b values.

Finally, for all of the 15 vegetable oils, table 6 shows the parameters that mark the average molecular size of the triglyceride mixtures and, therefore, that of FAME generated by them. In addition, there is the EF_{NR} value calculated on the C_{ME} determined for every analysed oil.

On the whole, most oils and, therefore, those related to FAME, have a similar average molecule size, with the exception of brassica and coconut oil which have a shorter and longer carbonaceous chain compared to average chains, respectively. Along with the figures of N_{CM} and N_S , the EF_{NR} oscillates between 0.78% and 1.20%. Figure 2 shows the relation between the latter parameter and the N_{CM} figure which emphasises the decrease of the non-renewability of the molecule due to the increase in the length of the carbonaceous chain, the non-renewability of the molecule decreases. This study has confirmed how the N_{CM} figure can be determined through a simple analysis such as saponification number. Figure 3 confirms

ME	ΔH_c (kJ/mol)	ΔH_r (kJ/mol)	$\Delta H_c - \Delta H_r$ (kJ/mol)	ΔE (%)	ΔH_i (kJ/mol)	ΔH_{iNR} (kJ/mol)	E_{NR} (%)
C ₇ H ₁₄ O ₂	4200	4246	-46.5	-1.1%	3960	95	2.4%
C ₉ H ₁₈ O ₂	5509	5526	-17.4	-0.3%	5159	95	1.8%
C ₁₁ H ₂₂ O ₂	6815	6806	9.4	0.1%	6357	95	1.5%
C ₁₃ H ₂₆ O ₂	8127	8086	41.4	0.5%	7556	95	1.3%
C ₁₅ H ₃₀ O ₂	9438	9366	72	0.8%	8754	95	1.1%
C ₁₇ H ₃₄ O ₂	10388	10646	-258	-2.5%	9952	95	1.0%
C ₁₉ H ₃₈ O ₂	11962	11926	36	0.3%	11151	95	0.9%
C ₂₁ H ₄₂ O ₂	13263	13206	57	0.4%	12349	95	0.8%
C ₂₃ H ₄₆ O ₂	14565	14486	79	0.5%	13548	95	0.7%
C ₂₅ H ₅₀ O ₂	Not taken	15766	---	---	14746	95	0.6%
C ₁₇ H ₃₂ O ₂	10548	10515	33	0.3%	9862	95	1.0%

TABLE 4 - Results of the thermochemical analysis on each ME.

Molecule	ΔH_c (kJ/mol)	ΔH_r (kJ/mol)	$\Delta H_c - \Delta H_r$ (kJ/mol)	ΔE (%)	ΔH_i (kJ/mol)	ΔH_{iNR} (kJ/mol)	E_{NR} (%)
C ₃ H ₈ O ₃	1657	1838	-181	-9.8	1675	27	1.6

TABLE 5 - Results of the thermo-chemical analysis on GL.

Derivation oil	Treatment	$N_{CM(ME)}$ (n)	N_S	EF_{NR}
Soya	Refined	18.8	196.4	0.87%
Sunflower	Refined	18.9	191.9	0.87%
Brassica carinata	Raw	21.0	177.4	0.78%
Coconut	Refined	14.1	259.9	1.20%
Rape	Refined	18.9	192.7	0.86%
Palm	Refined	18.1	200.6	0.90%
Grape seed	Raw	18.9	196.7	0.87%
Palm	Raw	18.0	201.6	0.90%
Corn	Raw	18.8	193.7	0.87%
Soya	Raw	18.8	197.8	0.87%
Rape	Raw	18.9	192.6	0.86%
Sunflower	Raw	18.9	194.7	0.86%
Jatropha	Raw	18.7	195.3	0.87%
Sunflower	Fried	18.9	194.3	0.87%
Cotton	Raw	18.5	200.8	0.89%

TABLE 6 - Values of N_{CM} , N_S and EF_{NR} for oils used for work.

this hypothesis and highlights an important analytic relation between the two parameters without using the gas-chromatographic analysis.

As a result of the previous correlations, N_S is capable of calculating the EF_{NR} value of a generic FAME (figure 4). The correlation obtained shows a very high R^2 value and covers a very important N_S field to which most of the FAME diffused on the market belongs.

4. Conclusion

The biofuel obtained from the triglyceride transesterification of vegetable oil, using methanol from fossil, englobes the non-renewable energy in its molecules originally released during combustion. The study has shown that for GL, the energetic supply is about 1.6% of the net energy obtained from combus-

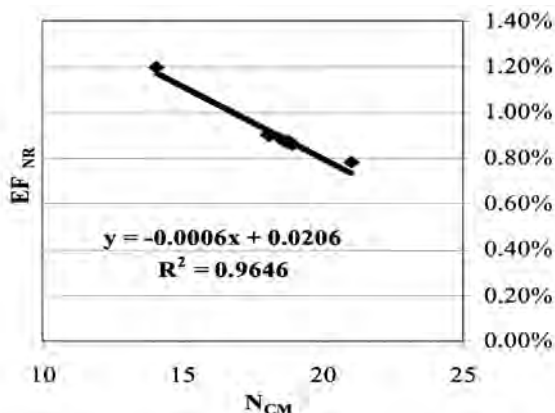


Fig. 2 - Correlation between EF_{NR} and N_{CM} of FAME.

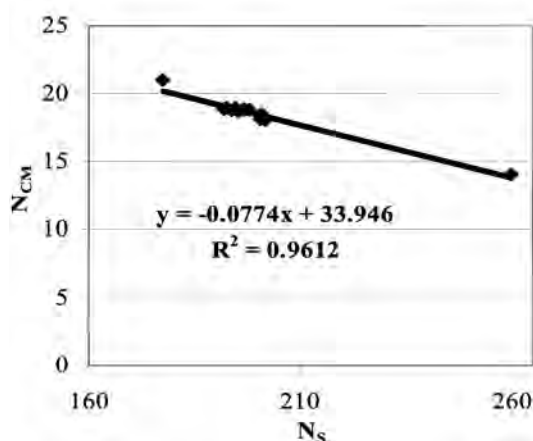


Fig. 3 - Correlation between N_{CM} and N_S .

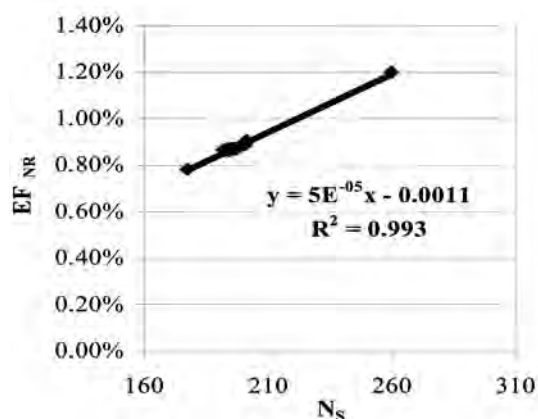


Fig. 4 - Correlations between EF_{NR} and N_S .

tion. In the case of FAME, the EF_{NR} value is conditioned by the length of the ME molecules. With the increase in the size of the average ME molecule, the EF_{NR} decreases. The study shows that through the N_S value, whose laboratory analytic definition is quite simple, it is possible to provide a rather precise estimation of the EF_N when FAME is obtained from various initial vegetal oils. On the whole, the most diffused FAME deriving, for example, from rape, soya

and palm oil have an EF_{NR} value lower than 1%. Nevertheless, it is assumed that the EF_{NR} value is unlikely to exceed the 1.5% threshold which corresponds to the products generated from vegetable oil with carbonaceous chain with an average of 10 carbon atoms. The data reported in this document can be a starting point for the identification of the correction factors for the fiscal aspects and the stimulation mechanism of renewable energy products.

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SUMMARY

Fatty acid methyl esters (FAME) and glycerol produced by transesterification reaction contain atoms that in the reagents belong to methanol and, therefore, are not renewable. A method to evaluate the content of the renewable and non-renewable energetic fraction, released during their combustion, was

developed using a thermochemical criteria, based on bond dissociation energies and the knowledge of the molecular structure of the reagents and the products. Results show that the fraction of non-renewable energy in the most diffused FAME is lower than 1% depending on the lengths of the carbonaceous methyl esters. Meanwhile, the energetic supply for the GL of this fraction is about 1.6%. The data reported in this document can be used to develop a criteria that corrects the fiscal mechanism aspects of some renewable energy products.

Keywords: Biodiesel, glycerol, renewable energy, bond enthalpy.

List of symbols

C_{ME}	percent composition of ME
ΔH_b	bond enthalpy
ΔH_r	reaction enthalpy
ΔH_i	low calorific value
ΔH_{NR}	enthalpy deriving from the part of the non-renewable molecule
ΔH_C	ΔH values obtained through experiments
EF_{NR}	fraction of non-renewable energy of FAME
N_S	saponification number
E_{NR}	fraction of non-renewable energy of the molecule
<i>FAME</i>	fatty acid methyl ester
<i>GL</i>	glycerol
H_E	evaporation enthalpy of water
<i>ME</i>	methyl ester
N_{CM}	average carbon atoms of FAME
N_C	carbon atoms of FAME