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GAS TURBINES AND BIODIESEL : A CLARIFICATION OF THE RELATIVE NO_x INDICES OF FAME, GASOIL AND NATURAL GAS

Pierre A. Glaude, René Fomet, Roda Bounaceur

DCPR, Nancy-Université, CNRS
1, rue Grandville - BP 20451 - 54001 NANCY Cedex – France

Michel Moliere

GE Energy Product-Europe,
20 avenue de Maréchal Juin, BP 379, 90007 Belfort, France

ABSTRACT

There is currently a sustained interest in biofuels as they represent a potential alternative to petroleum derived fuels. Biofuels are likely to help decrease greenhouse gases emissions and the dependence on oil resources. Biodiesels are Fatty Acid Methyl Esters (FAMES) that are mainly derived from vegetable oils; their compositions depend from the parent vegetables: rapeseed (“RME”), soybean (“SME”), sunflower, palm etc. A fraction of biodiesel has also an animal origin (“tallow”).

A key factor for the use of biofuels in gas turbines is their Emissions Indices (NO_x, CO, VOC, PM) in comparison with those of conventional “petroleum gasoils”. While biodiesels reduce carbon-containing pollutants, experimental data from diesel engines show a slight increase in NO_x. The literature relating to gas turbines is very scarce. Two recent, independent field tests carried out in Europe (RME) and in the USA (SME) showed slightly lower NO_x while a lab test on a microturbine showed the opposite effect.

To clarify the NO_x index of biodiesels in gas turbines, a study has been undertaken, taking gasoil and natural gas (NG) as reference fuels. In this study, a calculation of the flame temperature developed by the 3 classes of fuels has been performed and the effect of their respective compositions has been investigated. The five FAMES studied were RME, SME and methyl esters of sunflower, palm and tallow; these are representative of most widespread vegetable and animal oil bases worldwide. The software THERGAS has been used to calculate the enthalpy and free energy properties of the fuels and GASEQ for the flame temperature (T_f), acknowledging the fact that “thermal NO_x” represents the predominant form of NO_x in gas turbines. To complete the approach to structural effects, we have modeled two NG compositions (rich and weak gas) and three types of gasoil using variable blends of eleven linear/branched/cyclic molecules.

The results are consistent with the two recent field tests and show that the FAMES lie close to petroleum gasoils and higher than NG in terms of NO_x emission. The composition of the biodiesel and regular diesel fuel influences their combustion heat: methyl esters with double bonds see a slight increase of their T_f and their NO_x index while that of gasoil is sensitive to the aromatic content.

INTRODUCTION

Biomass-derived fuels can be used in many combustion equipments and may represent a valuable alternative to fossil fuels for reducing greenhouse gases (GHG). A key consideration for the success of any alternative liquid fuel is its emission signature in comparison with diesel oil which is the paradigmatic liquid fuel. In this respect, NO_x emission has a critical importance as far as gas turbines (GT) are concerned.

While a relatively high number of studies have been devoted to the combustion of biofuels in diesel engines, few work and scarce information are currently available for biofuels in gas turbine applications.

Diesel Engines: As far as diesel engines are concerned, two interesting reviews of the effect of FAME on emissions have been published recently [1]-[2]. Most works show a slight increase in NO_x emissions when using biofuels instead of conventional diesel fuel while some of them found that NO_x increases only in certain operating conditions. Some authors did not find any effect with respect to diesel fuel or even found a decrease in NO_x emissions when using biofuels. The increase in NO_x is mainly explained by an advanced injection time that is tied with the physical properties of FAMES. The higher compressibility bulk modulus of biofuels leads to a quicker pressure rise produced by the fuel pump which propagates towards the injectors [1][2]. Some authors investigated the influence of the type of biodiesel fuel. Graboski et al. [3] found that the NO_x

emission decreased when the mean carbon chain length increased and that the presence of double bonds impacted NO_x emissions: NO_x was found to increase linearly with the iodine number, which quantifies the number of multiple bonds in the fuel. The authors suggested that this effect could be due to differences in both physical and chemical properties of the FAMEs. Knothe et al. [4] compared pure methyl esters behavior in engines to conventional diesel fuel and found a decrease in NO_x with saturated C₁₂ and C₁₆ methyl esters while mono-unsaturated C₁₈ increased slightly the emission. The authors explained their results by a change in the adiabatic flame temperature. Based on numerical simulations of ideal reactors, Ban-Weiss et al. [5] proposed recently that the increase in the NO_x emission when using FAMEs would be due to higher flame temperature, especially when the fuel contains double bonds. The NO_x formation in such conditions is due to the thermal Zeldovich mechanism, which is predominant at high temperature. Their calculation are however based on C₃ and C₄ hydrocarbons, and methyl butanoate and methyl butenoate that are far to be representative of diesel or biodiesel fuels. Nabi et al. [6] calculated adiabatic flame temperature for a real diesel fuel and neem oil from the elementary C/H/O analyses of both fuels. They found that the Vegetable Oil had a slightly lower flame temperature than the conventional fuel.

Contrary to diesel engine where ignition time during the cycle is an important parameter, flame temperature is the essential driver for the NO_x emission in gas turbines.

Gas turbines:

As already stressed, there is a very reduced number of data available for the combustion of biodiesel in gas turbines.

In 2006, a field test has been performed on a 40 MW, E class gas turbine (Frame 6B) using a rapeseed methyl ester (RME), which led to the following emissions [7]:

- 247 mg/Nm³ on NG
- 367 mg/Nm³ on DF
- 360 mg/Nm³ on RME

In 2007, a similar field test has been performed on a 80 MW, E class gas turbine (Frame 7EA) with gasoil-soy methyl ester blends (SME) [8]. The results showed again a lower NO_x figure with BF3 which was about 83% that of DF. Since numerous papers published by the diesel engine community pointed higher NO_x with biodiesel, it was considered rather necessary to clarify these isolated results.

On the other hand, a recent comparison of biofuel and diesel distillate #2 in a microturbine generator (30kW Capstone C30) showed an increase in NO_x emissions by switching from gasoil to biofuel [9]. The most sensitive parameter seems to be a change in the atomization patterns of the fuel.

NUMERICAL APPROACH

In order to elaborate a rational statement about the NO_x indices of biodiesel and diesel fuel, a thermochemical approach has been used to evaluate the adiabatic flame temperatures. NO_x production is directly linked to temperature and this parameter allows a simple comparison of the different fuels, whatever the real combustion device is. The following fuels were investigated:

- individual chemical compounds belonging to the

chemical families involved in gas turbine fuels in order to assess the influence of each chemical family,

- various FAME blends that are representative of the most common biodiesel productions worldwide,
- various blend models representative of petroleum gasoil,
- various natural gas compositions.

This approach was intended to get at the same time (i) a comparison of the emission indices of the different fuel classes (ii) an analysis of the influence of their chemical structures on flame temperature and thus on NO_x emission.

Composition of Biodiesel fuels (FAME)

The world production of vegetable oil ("VO") is rapidly increasing and has been estimated to 101 Mt in 2003, when it reached only 86 Mt in 1999. Estimations are around 130 Mt for 2010. Another important production of fat material is 20 to 25 Mt of animal greases per year [10]. Soybean oil is the main production (more than 30% of the total amount), with palm oil (ca 28%). Rapeseed and sunflower oils are the next important productions, around 13% and 9%, respectively. Soybean and palm oil have enjoyed the most important production increases during the past years. Regional specificities can be noted: soybean oils are produced in America while sunflower and rapeseed are essentially produced in Europe and palm oils in Asia. VOs essentially consist of triglycerides, i.e. triesters of glycerol and fatty acids. Table 1 displays the proportions of the different fatty acids that are contained in these four major VOs. As far as animal greases are concerned, five categories can be distinguished: lard from pigs, tallow from bovines and sheeps, poultry grease and fish oils. The latter cannot be used in combustion because of its high content of unsaturated molecules that causes the formation of gums and polymers.

Table 1: Typical composition of fatty acids in VOs (wt%) [10].

	VO1 Rapeseed	VO2 Sunflower	VO3 Soybean	VO4 Palm
C14:0				1
C16:0	5	6	10	44
C18:0	2.5	5	4	6
C18:1	59	18	23	38
C18:2	21	69	53	10
C18:3	9	<0.5	8	<0.5
C20:0	<0.5	<0.5	<0.5	<0.5
C20:1	1	<0.5	<0.5	
C22:0	<0.5	1	<0.5	
C22:1	1			

Table 2: Compositions of the 5 selected biodiesels (% mol) (BF1 to 4 derive from the VO1 to 4 of table 1; BF5 from tallow)

Name	Formula	BF 1 Rapeseed	BF 2 Sunflower	BF 3 Soybean	BF 4 Palm	BF 5 Tallow
myristic acid	C 14:0	0	0	0	1	4
palmitic acid	C 16:0	5	6	10	44	27
stearic acid	C 18:0	3	5	4	6	24
oleic acid	C 18:1, Δ9	59	18	23	38	40
linoleic acid	C 18:2, Δ9,12	21	69	53	10	3
linolenic acid	C 18:3, Δ9, 12, 15	9	1	8	0.5	0.5
arachidic acid	C 20:0	0.5	0.5	1	0.5	0.5
gadoleic acid	C 20:1, Δ9	1	0.5	0.5	0	1
behenic acid	C 22:0	0.5	0	0.5	0	0
erucic acid	C 22:1, Δ13	1	0	0	0	0

However, due to their natural origin, vegetable oils also contain cholesterol, fatty alcohols that can be free or esterified by fatty acids, and other minor compounds [11] that can be classified as follows, by decreasing content:

- triglycerides (or triesters of fatty acids),
- free fatty acids,
- minor components (sterols, phospholipids...)
- traces of metals (calcium, potassium...)

Some of these components can create operational issues in thermal equipments; in addition, vegetable oils are generally very viscous fluids. Therefore, while they can be used as raw products in boilers, VO are often processed to produce biodiesel that suit better the operational constraints of diesel or gas turbine engines. For that purpose, a transesterification reaction transforms the heavy triglycerides into monoesters of methanol: the Fatty Acid Methyl Ester. Interestingly FAMES have physical and thermal properties (viscosity, LHV) close enough to that of petroleum diesel for a use in combustion without significant hardware modifications. Based on Table 1, four VO-derived biodiesels will be considered in this study; they are representative of the most important biodiesel classes worldwide. Table 2 displays the composition of these mixtures. Tallow and lard consist mainly of C₁₄ to C₂₀ fatty acids but contain higher proportions of saturated acids than VOs. Typically, they involve more than 50% of saturates and less than 5% of polyunsaturated acids, which explains that they have a higher viscosity than VO-derived FAMES. Based on a typical composition of tallow [12], the fifth case (BF5) can be taken as representative of a biodiesel yielded by the transesterification of an animal grease.

Compositions of Conventional Diesel Fuels (“DF”)

Table 3 summarizes the 3 blends (DF1 to 3) selected as models for petroleum diesels. Diesel fuels are actually complex mixtures of hundreds of molecules, most of them containing from 7 to 15 carbon atoms. Since modeling in detail such blends is currently unpractical, synthetic mixtures have been proposed in the literature. Although n-heptane has been widely modeled [13], its chemical and physical properties remain far from a real diesel fuel. A more refined blend model (DF1) has been recently proposed which contains four linear, branched and cyclic molecules [14] that account for all the chemical families involved in a real diesel fuel used in engines. Another representative surrogate (DF2) is proposed based on the analysis of a commercial diesel fuel

[15]. A single molecule represents each chemical family; C₁₀ isomers are considered as the most representative molecular weights. One can note that for a conventional diesel fuel, H/C is in the range of 1.9-2.1 [15]. A last blend (DF3) represents a non conventional gasoil called Light Cycle Oil (LCO), that is rich in aromatic and polycyclic molecules [16]. In this case, C₁₄ isomers are considered since the mean molecular weight is higher for this type of fuel.

Table 3: Composition of the synthetic diesel fuels (mol%)

Name	Formula	DF 1	DF 2	DF 3
n-decane	n-C ₁₀ H ₂₂		31	
n-tetradecane	n-C ₁₄ H ₃₀			14
n-hexadecane	n-C ₁₆ H ₃₄	23.5		
n-propyl cyclohexane (PCYH)	C ₉ H ₁₈	26.9		
n-butyl cyclohexane (BCYH)	C ₁₀ H ₂₀		39	
n-propyl benzene (PBZ)	C ₉ H ₁₂	22.9		
n-butyl benzene (BBZ)	C ₁₀ H ₁₄		16	
n-octyl benzene (OBZ)	C ₁₄ H ₂₂			29
naphthalene (NP)	C ₁₀ H ₈	7.7		
α-methyl naphthalene (MNP)	C ₁₁ H ₁₀		14	
α-butyl naphthalene (BNP)	C ₁₄ H ₁₈			55
H/C ratio		1.86	1.80	1.51

Compositions of Natural Gas fuels (“NG”)

The composition of commercial natural gas depends on the production field and actually from the particular extraction well it stems from. In particular, NGs can contain different amounts of hydrocarbons heavier than methane that impact on their LHV. Two NG compositions have been considered that correspond to pure methane gas and to a “rich gas” [17] respectively. They are displayed in Table 4.

Table 5 : Ideal gas phase thermodynamics properties

$\Delta_f H_{298K}^\circ$ is expressed in kcal.mol⁻¹ and S_{298K}° and $C_p^\circ(T)$ are given in cal.mol⁻¹.K⁻¹.

Species	$\Delta_f H_{298K}^\circ$	S_{298K}°	$C_p^\circ(T)$						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
N ₂	0.00	45.77	6.95	7.01	7.08	7.19	7.50	7.83	8.32
CH ₄	-17.92	44.52	8.49	9.81	11.15	12.50	15.13	17.43	21.07
C ₂ H ₆	-20.29	54.85	12.59	15.76	18.67	21.31	25.80	29.37	36.24
C ₃ H ₈	-24.88	64.51	17.64	22.60	26.99	30.85	37.10	41.83	49.95
C ₄ H ₁₀	-30.23	74.12	23.36	29.69	35.31	40.25	48.24	54.24	64.51
n-C ₁₀ H ₂₂	-59.81	129.96	56.05	71.35	84.71	96.29	114.75	128.16	149.00
n-C ₁₄ H ₂₀	-79.62	167.35	77.94	99.18	117.69	133.68	159.11	177.51	205.99
n-C ₁₆ H ₃₄	-89.49	186.10	88.88	113.06	134.14	152.35	181.27	202.13	234.41
PCYH	-45.40	99.73	43.36	58.44	71.56	82.89	100.78	113.48	131.56
BCYH	-50.35	109.07	48.86	65.38	79.80	92.25	111.89	125.81	145.82
PBZ	1.91	95.61	36.28	47.53	57.18	65.38	78.03	86.74	99.77
BBZ	-3.38	104.76	42.07	54.85	65.81	75.13	89.50	99.43	114.54
OBZ	-22.83	142.37	63.65	82.30	98.39	112.12	133.48	148.40	170.97
NP	35.91	82.35	31.99	42.94	52.06	59.58	70.73	78.26	93.19
MNP	28.24	92.58	37.14	49.34	59.65	68.27	81.32	90.25	105.91
BNP	13.13	119.41	54.44	70.57	84.59	96.59	114.95	126.67	133.62
C14:0	-157.81	192.42	87.49	109.90	129.63	146.74	173.56	191.28	201.94
C16:0	-167.70	211.13	98.44	123.81	146.10	165.43	195.74	215.94	230.42
C18:0	-177.60	229.85	109.37	137.73	162.59	184.12	217.90	240.60	258.92
C18:1	-149.48	226.47	104.94	132.69	157.02	178.07	210.95	232.85	249.88
C18:2	-120.84	224.25	101.97	128.98	152.66	173.14	205.10	226.31	241.97
C18:3	-92.20	222.02	99.00	125.28	148.30	168.20	199.25	219.78	234.02
C20:0	-187.49	248.56	120.34	151.59	179.04	202.82	240.10	265.22	287.41
C20:1	-159.38	245.18	115.87	146.60	173.50	196.75	233.12	257.52	278.38
C22:0	-197.38	267.27	131.27	165.52	195.53	221.50	262.26	289.90	315.91
C22:1	-169.27	263.90	126.82	160.51	189.98	215.44	255.29	282.17	306.87

Table 4 : Composition of the natural gas fuels (mol%)

Formula	NG 1	NG 2
	Alaska	Libya
CH ₄	100	70
C ₂ H ₆		15
C ₃ H ₈		10
C ₄ H ₁₀		4
N ₂		1

CALCULATION METHOD

Thermochemical data

The thermochemical data used in the calculation of the adiabatic flame temperature of the different fuels have been computed by using the software THERGAS [18] and based on the group additivity method proposed by Benson [19]. The data used herein for the group contributions are mostly those proposed by Domalski and Hearing [20]. Since most of the natural unsaturated fatty acids have a cis conformation of their double bond, all FAMES have been considered as cis isomers (a cis double-bond induces an enthalpy of 1 kcal mol⁻¹ higher than a trans double bond which is quite insignificant). Table 5 summarizes the standard data in gas

phase calculated at 298 K for species involved in the surrogate fuels studied here.

Flame temperature calculation

The adiabatic flame temperature (T_f) at constant pressure is evaluated by calculating the temperature at which the enthalpy of the combusted air/fuel mixture is minimal, air and fuel being considered as perfect gases. The calculation is performed using the software GASEQ developed by C. Morley [21]. The method is based on the minimization of the Gibbs Free Energy G of the mixture at constant pressure by fixing a set of reaction products. The temperature is adjusted iteratively until the equilibrium composition has an enthalpy which is the same as that of the reactants. No chemical equation is thus necessary.

The proportions of nitrogen, oxygen and argon in air are 0.7809, 0.2095, and 0.0096, respectively. Species considered for the equilibrium calculation are Ar, N₂, H₂O, CO₂, CO, O₂, OH, H, O, H₂, and NO.

Adiabatic flame temperatures under 1 atm with fresh gases at 300 K were first calculated for molecules of each chemical family present in conventional diesel fuels or in biofuels.

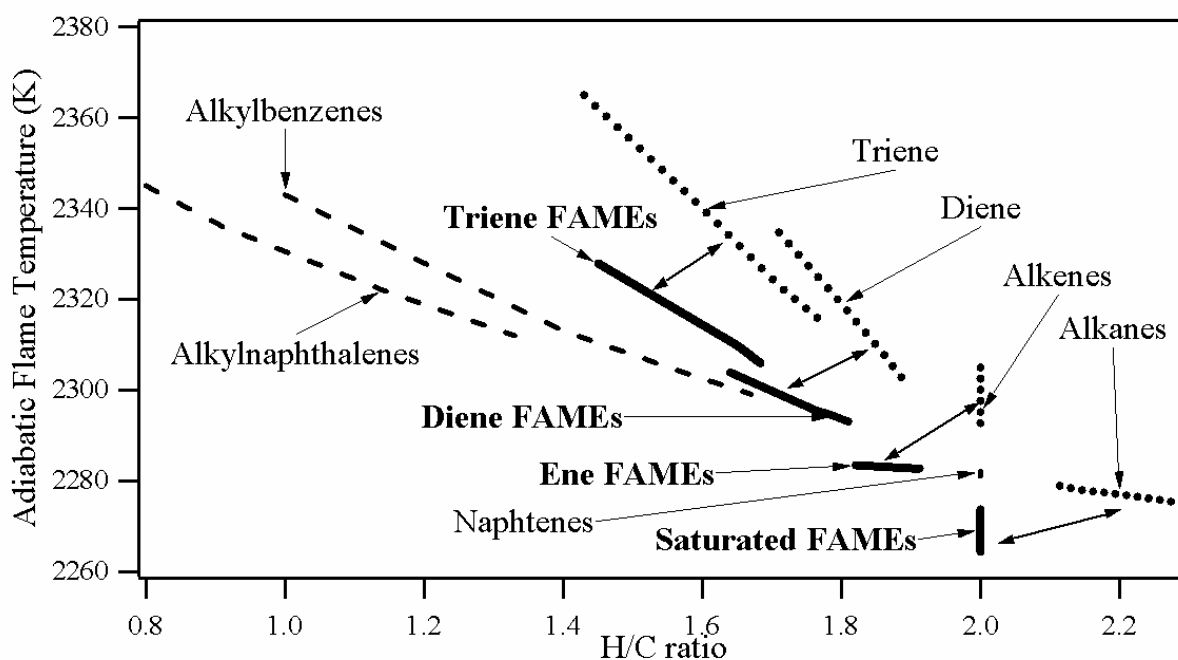


Figure 1: Adiabatic flame temperatures of chemical species contained in fuels as a function of H/C ratio

These calculations allowed to compare the range of temperatures that are reached by the various chemical families and to quantify the influence of the composition on the flame temperature and then on the NO_x index. For each surrogate mixture defined above, three calculations have been performed:

- **Case 1:** a standard case considering a stoichiometric mixture of combustible in air, at 300 K under 1 atm. These conditions are far from gas turbine conditions but comparable with data from other sources.
- **Case 2:** a case representative of an F-class gas turbine, i.e. a stoichiometric mixture under a temperature of 400°C (673 K) and a pressure of 16 atm.
- **Case 3:** a standard gas turbine case, representative of an E-class, i.e. a stoichiometric mixture, under a temperature of 350°C (623 K) and a pressure of 11.5 atm.

Note that these calculations does not allow any prediction of the NO_x emission in a real gas turbine, but only of a trend when substituting a fuel to another.

RESULTS AND DISCUSSION

1. Parametric Study of T_f

Figure 1 displays the adiabatic flame temperature calculated in Case 1 for molecules of different chemical families as a function of the H/C ratio. Focusing first on diesel fuels, species containing between 10 and 20 carbon atoms were studied, plus benzene. Aliphatic alkanes, alkenes, dienes, and trienes were investigated, such as alkylcyclohexanes, alkylbenzenes, and alkyl naphthalene as components of conventional gasoils. In the case of FAMES, temperatures were calculated for linear saturated methyl esters, and for those containing one, two, and three double bonds. The results show that T_f increased when unsaturated bonds were

present in the molecule, while the H/C ratio decreased. T_f rises from alkanes to trienes, and from saturated FAMES to FAMES containing three double bonds. A key result of these calculations is that FAMES have always lower T_f data than the corresponding hydrocarbons (carbon chain without an ester function) because the oxygenated function in which the carbon atom is already oxidized decreases the enthalpy of reaction (see arrows in figure 1). In other terms, the presence of the ester function, in which a carbon atom is already bound to two oxygen atoms within a carboxylic group, adds virtually nothing to the heat of the combustion and a methyl ester involving N carbon atoms has about the same thermal effect (and the same stoichiometric air consumption) as a similar hydrocarbon involving (N-1) carbon atoms. This equals to say that a (1/N) fraction of the carbon content of the FAME molecule is already oxidized and is “lost” for the generation of heat. At the same time, the CO₂ molecule generated by this carboxylic group tends to decrease T_f as it consumes sensible heat among the reaction products. This is the key explanation of the systematically lower T_f data of FAMES as compared with gasoil of equivalent composition. FAMES with aromatic chains have not been modeled in this work but would have shown the same effect; such FAMES are not representative of normal biodiesels, except for those deriving from used frying oil (yellow greases) and having undergone strong pyrolysis.

Alkylbenzenes and alkyl naphthalenes lead to high T_f values and low H/C ratio. The T_f data of naphthenes (here: alkylcyclohexanes) are not sensitive to the size of the alkyl group and remain close to 2281 K, with a H/C ratio of 2. It is worth noting that all lines are converging toward the point ($T_f = 2281$ K; H/C = 2) when the carbon atom number increases since C_nH_{2n} is the limit formula for all studied

chemical families when the alkyl group grows in length i.e. when n becomes infinite, whereby overwhelming the weight of the other chemical functions. This limit case that corresponds to $H/C = 2$ gives $T_f = 2281$ K. Methane and other components of natural gas were not represented in the figure to avoid wider scales. Methane leads to $T_f = 2226$ K and $H/C = 4$, ethane to 2259 K and 3, respectively.

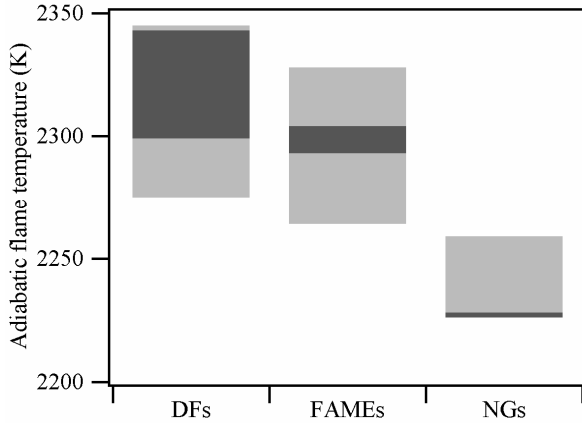


Figure 2: Range of adiabatic flame temperature of fuels

Real fuels involve different proportions of each classes, with an average H/C ratio of 1.8. Figure 2 summarizes the temperature range reached by the components of the different fuels of interest in gas turbines, i.e. diesel fuels (DFs), biofuels (FAMEs), and natural gas (NGs). The darker area delimits the T_f range of what can be considered the most usual composition range of each fuel class: alkylbenzenes for DFs, unsaturated methyl esters with two double bonds for FAMEs and methane for NG. It appears that the flame temperature of DFs and FAMEs are close even though DF tend to have higher values. The composition of fuels is very sensitive: a gasoil rich in alkanes and naphthenes could have a lower flame temperature than a very unsaturated biofuel. Reversely, an increasing proportion of aromatic species in the diesel fuel will dramatically increase the flame temperature. However, natural gas fuels have always lower T_f data even when they contain significant amounts of C_{2+} alkanes.

2. T_f data of the fuel selection

Table 6 gives the calculated values of the adiabatic flame temperatures (T_f) for the complex mixtures studied as surrogates of the real fuels: the 5 FAMEs, the 3 DFs and the 2 NGs.

a) NG fuels: Natural gas fuels lead to lower T_f values than diesel fuels as their higher H/C ratio implies a lower enthalpy of combustion than that of heavier molecules. NG2 contains alkanes heavier than methane and leads then to higher T_f values than NG1.

b) DF fuels: The 3 diesel fuel compositions lead to close values of T_f . DF2, the second surrogate for commercial diesel fuel, contains a little bit more of diaromatic molecules than DF1 and leads to slightly higher temperatures. DF3 represent a heavier blend such as LCO and is rich in aromatics and

polycyclic molecules. It leads to the highest temperature and induces the worse NOx index.

c) BF fuels: Biodiesel fuels lead to adiabatic flame temperature data that are higher than those for NG and close to those of DF. This outcome is consistent with calculations performed for single molecules and with the recent results procured by the above-mentioned field tests. As compared with DFs, usual biodiesel fuels lead to equal or slightly lower T_f values when comparing to diesel fuels. The five biofuels have a very similar behavior. In particular, there is a limited difference between FAMEs obtained from rapeseed (BF1) and soybean (BF3). A larger amount of unsaturated bonds increases however slightly the enthalpy of combustion. BF2 and BF3 contain the largest amounts of insaturated bonds and lead to the highest $T_{f,ad}$ values while BF4 (palm oil) and BF5 (tallow) lead to smaller $T_{f,ad}$ values due to their higher content of saturates (C_{16} and C_{18}).

In summary, FAMEs have a level of LHV equal or lower than conventional diesel fuels and, within the FAME family, the LHV of BF4 and BF5 have the lowest ones; T_f follows the same trend as the LHV.

Table 6: Adiabatic flame temperatures (T_f), at constant pressure, in Kelvin, for the different fuels

	Case 1	Case 2	Case 3
BF 1	2287	2556	2519
BF 2	2291	2559	2522
BF 3	2290	2558	2521
BF 4	2279	2547	2510
BF 5	2278	2546	2509
DF 1	2290	2558	2521
DF 2	2292	2560	2523
DF 3	2309	2578	2541
NG 1	2227	2449	2454
NG 2	2245	2509	2470

BF: biofuel, DF, diesel fuel, NG: natural gas.

The overall results obtained for realistic mixtures contradict those of Ban-Weiss et al. [5], who proposed higher adiabatic flame temperatures for biofuels than for conventional diesel fuel but compared in fact small FAMEs to small alkanes, without considering the large amount of unsaturated species contained in a diesel fuel, especially aromatics and naphthenoaromatics. On the other hand, our results are in accordance with those of Nabi and al. calculated from the elementary analyses of a diesel fuel and a neem oil [6].

CONCLUSIONS

This study was intended to clarify the question of how biodiesel impacts on the NOx emission of gas. The adiabatic flame temperature T_f represents the highest temperature that a combustion can produce for a specific mixture whatever the combustion device. Thus, T_f can be considered as the major determinant of NOx emissions in gas turbine and has been taken as criterion.

Calculations of T_f for various types of molecules contained in biodiesels, gasoil and natural gas and for surrogate fuel mixtures allowed to rank these 3 fuel classes and to point out interesting effects within each fuel class.

The results show that diesel fuels tend to generate the highest temperatures, natural gas the lowest and biodiesel lie in-between. The variability of the composition of gasoils can substantially change flame temperature, while biofuels are less sensitive to composition variations.

This ranking complies with the finding of two recent field tests that show, for gas turbines, a slight decrease of NO_x when passing from gasoil to biodiesel. They highlight a main difference between gas turbines and diesel engines for which the trend is reversely an increase of NO_x when switching from petroleum diesel to biodiesel.

The calculations performed with variable FAME distributions show no significant effect on the exothermicity of the combustion and thus on NO_x. This result is interesting as it tends to predict an even behavior of biodiesels worldwide. It must be stressed that the conclusions of this approach are valid for invariant combustion conditions (constant geometry and air distribution in combustion chambers; unchanged fuel nozzle sizes and atomization conditions; prompt and organic NO_x neglected). Finally OEM's shall be consulted for an authorized statement on actual emissions.

REFERENCES

- [1] Lapuerta M., Armas O., and Rodriguez-Fernandez J., 2008, "Effect of biodiesel fuels on diesel engine emissions", *Progress in Energy and Combustion Science*, **34**, pp. 198-223.
- [2] Szibist J., Song J., Alam M., Boehman A., 2007, "Biodiesel combustion, emissions and emission control", *Fuel Processing Technology*, **88**, pp. 679-691.
- [3] Graboski M.S., McCormick R.L., and Alleman T.L., Herring A.M., 2003, "The effect of biodiesel composition on engine emission from a DDC series 60 diesel engine", *National Renewable Energy Laboratory*, NREL/SR-510-31461.
- [4] Knothe G., Sharp C.A., and Ryan III T.W., 2006, "Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine", *Energy Fuels*, **20**, pp. 403-408
- [5] Ban-Weiss G.A., Chen J.Y., Buchholz B.A., and Dibble R.W., 2007, "A numerical investigation into the anomalous slight NO_x increase when burning biodiesel: a new (old) theory", *Fuel Processing Technology* **88**, pp. 659-667
- [6] Nabi N., Akhter S., and Mhia Z.S., 2006, "Improvement of engine emissions with conventional diesel fuel and diesel-biodiesel blends", *Bioresource Technology*, **97**, pp. 372-378.
- [7] Molière M., Panarotto E., Aboujaib M., Bisseaud J.M., Campbell A., Citeno J., Maire P.A., and Ducrest L., 2007, "Gas turbines in alternative fuel applications: biodiesel field test" *ASMEE Turbo Expo 2007*, May 14-17, Montréal, Canada; GT2007-27212
- [8] Duke Energy Carolinas and GE Energy Successfully conduct first-of-a-kind biodiesel field tests; July 17, 2007
<http://www.dukeenergy.com/news/releases/2007071701.asp>
- [9] C.D. Bolszo, V.G. McDonell, 2009, "Emissions optimization of a biodiesel fired gas turbine", *Proc. Combust. Inst.*, in press, doi: 10.1016/j.proci.2008.07.042
- [10] Ballerini D., and Alazard-Toux N., 2006, *Les biocarburants, état des lieux, perspectives & enjeux du développement*, TECHNIP Edition.
- [11] Karleskind A., 1992, *Raffinage des corps gras*, In: *Manuel des Corps Gras Vol. 2* Lavoisier 1992, pp. 789-880.
- [12] Institut Technique d'Etude et de Recherche sur les corps Gras, ITERG, <http://www.iterg.com/>
- [13] Colin, O., Pires da Cruz A., and Jay, S., 2005, "Detailed chemistry-based auto-ignition model including low temperature phenomena applied to 3-D engine calculations" *Proceedings of the Combustion Institute*, **30**, pp. 2649-2656.
- [14] Mati, K., Ristori, A., Gail, S., Pengloan, G., and Dagaut, P., 2007, "The oxidation of a diesel fuel at 1-10 atm: Experimental study in a JSR and detailed chemical kinetic modelling", *Proceedings of the Combustion Institute*, **31**, pp. 2936-2646.
- [15] Guibet J.C., 1997, *Carburants et Moteurs*, p. 46, Edition Technip, Paris.
- [16] Molière M., Geiger F., "Gas Turbines in alternative fuel applications: The utilization of highly aromatic fuels in power generation", *ASMEE Turbo Expo 2003*, GT2003-53272.
- [17] Baukal, C.E., 2001, in *The John Zink Combustion Handbook*, p 159, CRC Press.
- [18] Muller, C., Michel, V., Scacchi, G., and Côme, G.M., 1995, "THERGAS: a computer program for the evaluation of thermochemical data of molecules and free radicals in the gas phase", *Journal de Chimie Physique*, **92**, pp. 1154-1178.
- [19] Benson, S.W., 1976, *Thermochemical kinetics*, 2nd ed. John Wiley, New York.
- [20] Domalski E.S. and Hearing E.D., 1993, "Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K", *Journal of Physical and Chemical Reference Data*, **22**, pp. 805-1159.
- [21] Morley, C., *Gaseq, Chemical equilibria in perfect gases*, v. 0.79, <http://www.gaseq.co.uk>