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Thermal characterization of a biodiesel nitration: bio-additive's synthesis by calorimetric methods

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Abstract

The aim of this study was to synthesize a substitute to the 2-Ethyl Hexyl Nitrate (EHN) by nitrating a biodiesel. EHN is commonly used to improve the auto-ignition properties of diesel fuels. The biodiesel was obtained by trans-esterification of canola oil. The nitration reaction was carried out in a reaction calorimetry RC1 with semi-batch mode to study its exothermic behavior. Mixed sulfuric/nitric acid was used as nitrating agent. The impact of the synthesis temperature on the thermal behavior and on the reaction medium composition was investigated. The final product was analyzed by using several analytical techniques such as iodine number, infrared spectrometry, GC-MS and mass spectrometry. This analytical study combined with the results of thermal stability study in DSC, allowed to highlight that chemical transformations play an important role on the thermal reaction behavior and on the Maximum Temperature of the Synthesis Reaction (*MTSR*). In addition to the mixed acid decomposition, the synthesis at high temperature involves the production of nitrated products: methyl-8-nitro oleate, methyl-10-nitrate stearate, methyl-10-nitrate-9-nitrostearate. Also, the Cooperative Fuel Research (CFR) engine was used to analyze the cetane number of diesel fuel mixed with our additive according to the ASTM D613 standard. The results showed an increase in cetane number of 3.2 points.

Keywords: methyl oleate, cetane number, reaction calorimeter, DSC, *MTSR*

1 Introduction

The industrialization and motorization in recent years come along with a high demand for petroleum products and an increase in air pollution [1]. It has been established by the Interprofessional Center for Technical Studies of Atmospheric Pollution (CITEPA), in France, that the automotive sector (mainly diesel engines) plays a leading role in air pollution (CO_2 , CO , NO_x , SO_2).

To reduce the pollution related to diesel engines, several solutions have been tested including the setting up of catalytic oxidation pots, particles filters [2] and the use of additives, mainly cetane number improvers [3].

Cetane improver additives are commonly used to increase engine performances. According to Beatrice et al 1996 [4], an increase in the cetane number reduces NO_x and particle emissions. There are a lot of cetane number improvers [5] [6] but the 2-EthylHexyl Nitrate (EHN) is the main additive used for diesel. The EHN is an energy molecule obtained by nitration of iso-octanol (fossil fuels) with mixed nitric/sulfuric acid (1:1.5 w/w).

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Several studies showed that the iso-octanol nitration is a strongly exothermic reaction which takes place in a heterogeneous liquid-liquid mixture [7] [8]. EHN additive is thermally unstable and sensitive to heat. Its thermal instability is mainly due to energetic functional groups like nitro (C–NO₂) and nitrate (C–O–NO₂). Those functional groups are composed of easily broken C–N covalent bonds. In fact, according to Yang et al 2014 [9], several industrial accidents in China are due to the loss of control during the EHN synthesis. The thermal behavior of this reaction need to be carefully investigated to assess the associated risks [10].

With the scarcity of fossil fuels, it is important to reduce the dependency on petroleum products. The goal of the work described in this article is to synthesize a substitute to the EHN by nitrating a trans-esterified vegetable oil (biodiesel). Many studies on the use of biodiesel as biofuels [11][12] or as bio-additive [13] have been realized over the years. The biodiesel's particularity is that it contains less carbon, less sulfide, less water and more oxygen atoms than fossil diesel. Therefore, it is less dangerous for humans [14] and its amount of oxygen atoms improves combustion [15].

In this article, the biodiesel obtained from canola oil was used. According to Abdullah et al 2010 [16], the presence of double bonds favors the nitration reaction. And the canola oil has a lot of double bounds compared to the other vegetable oils. The classic mixed sulfuric/nitric acid [17] (1.5:1 w/w) was used as the nitrating agent.

First, a study about the identification and the characterization of the chemical compounds that results from nitration by various analytical techniques (infrared spectrometer, GCMS, electro spray ionization mass spectrometer, and iodine index measurement) was conducted. Then, a complete study on the thermal stability of the reaction mixture (reagents and products) was realized. This study uses the thermal information given by a reaction calorimeter RC1 and a DSC type microcalorimeter. The quality of the synthesized bio-additive was determined by measuring its cetane number according to the ASTM standard D 613.

2 Materials and products

2.1 Products

The biodiesel (Diester®) used was obtained by trans-esterification of canola oil and was provided by Saipol company (Grand-Quevilly-France). Nitric (65%w/w), sulfuric (95% w/w) acids used as nitrating agent and solvents (potassium iodide 1% volumetric, sodium thiosulfate (Na₂S₂O₃) 0.1M, bicarbonate solution for analysis (>99.7%) and Wijs reactive 0.1 mol·L⁻¹) are provided by Fisher Chemical. The methyl nonadecanoate (> 98%) for GC analysis was supplied by Sigma Aldrich.

2.2 Materials

▪ Calorimetric reactor RC1-RTCal

The nitration was carried out in a calorimetric reactor RC1-RTCal (Mettler®) operating in semi-batch mode. It is equipped with an AP00-0.5-RTCal reactor vessel with 0.5L capacity. Mixing system is made of an impeller with one baffle. The experimental device is presented

in Fig. 1. The reactor has a temperature control system (between -20°C and $+165^{\circ}\text{C}$) and an *RTCal* measurement technology based on thermal flow sensors located on the reactor wall. The temperature regulation includes a thermostatic group which takes care of the various regulation modes thanks to a fluid (Rodorsil 47 V20). This device provides real-time monitoring of the heat released by the nitration reaction which is highly exothermic.

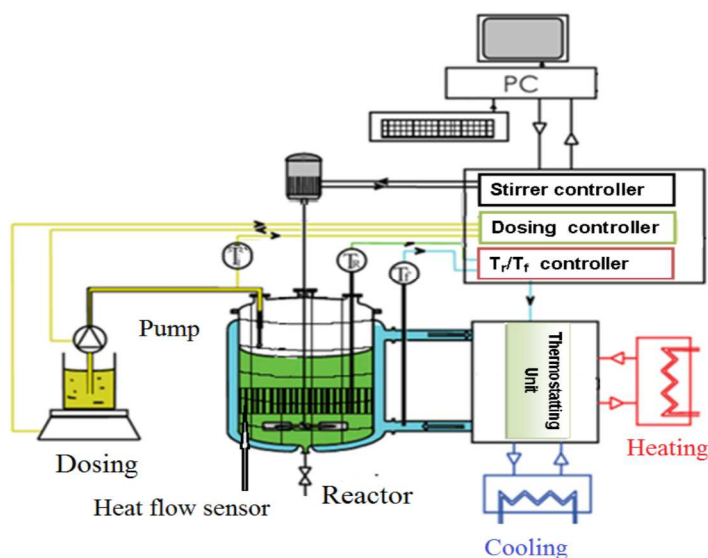


Fig. 1. Reaction calorimeter RC1-RTCal (Mettler®)

▪ Differential Scanning Calorimeter DSC Q20

The reactive and products stability study was based on thermograms analysis obtained with the DSC Q20. The DSC was provided by TA Instruments with purge using extra pure nitrogen ($50 \text{ mL}\cdot\text{min}^{-1}$). It can work in isothermal and non-isothermal conditions. DSC measures temperature with accuracy of $\pm 0.05 \text{ K}$. Its specific sensitivity is $1\text{mW}\cdot\text{kg}^{-1}$ [18]. The device detects temperature changes between the sample and the reference to measure heat flow over time and temperature. Gold-plated high pressure crucibles (M20 crucibles from Swiss Institute for the Promotion of Safety and Security) were used for measurement [19].

▪ Chemical analysis materials

The FTIR IR Affinity-1S from Shimadzu (400 to 4000 cm^{-1}), GC-MS from Agilent technology 7890A GC/5975C VL MSD, and the mass spectrometry with electro spray ionization from Waters LCT Premier were used to identify and quantify chemical species.

GC-MS analyses were performed in a GC6850 gas chromatography coupled with a 5975C MSD Quad Instrument with electrons impact ionization at 70 eV . A HP5-MS 5% Phenyl Methyl Siloxane capillary column (Agilent 19091S-433E) with a 0.25 mm i.d., 30 m nominal length and $0.25 \mu\text{m}$ phase film diameter was used. The carrier gas was helium at a flow rate of $15 \text{ mL}\cdot\text{min}^{-1}$.

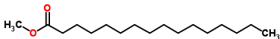
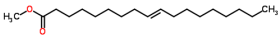
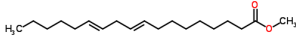
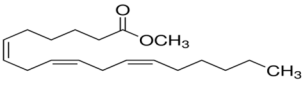
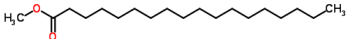
3 Synthesis and chemical analysis

3.1 Experiment

Considering the chemical instability of the mixed acid (nitrating agent), it was prepared just before the synthesis reaction (nitration). 86.4 g of sulfuric acid was introduced with a flow rate of $4\text{g}\cdot\text{min}^{-1}$ into the reaction calorimeter filled with 57.6 g of nitric acid. The mixture was stirred at 200 rpm and kept at 5°C during the addition. At the end, the mixture, composed of HNO_3 27 %, H_2SO_4 58%, H_2O 15% (w/w), was kept in the fridge at the same temperature.

To carry out the synthesis reaction, 144g of mixed acid was dosed with a flow rate of $4\text{g}\cdot\text{min}^{-1}$ into the reactor initially filled with 150 g of biodiesel composed of 92% of methyl oleate (determined by GC-MS Table 1). These operating conditions are chosen after preliminary study on the effect of parameters such as a flow rate, stirring speed on thermal behavior in order to ensure the safe operation of the reactor. The synthesis reaction was carried out at 600 rpm stirring speed, in the isothermal mode. This experiment was realized at seven different temperatures (10-15-20-25-30-40 and 50°C). The Mettler RC1 operating software allows to record the thermal signal (power profile) and to monitor the reaction progress. The final product was then transferred to a separating funnel and separated in two phases. Only the organic phase (which contains the nitrated products) was analyzed. Before the analysis, the organic phase was, first, washed with a bicarbonate solution at 2% w/w, and then with distilled water until a neutral pH was obtained.

Table 1: Fatty Acid Methyl Esters (FAME) from canola composition

Compounds	% w/w
Methyl palmitate	
	2.2
Methyl oleate	92.0
	
Methyl linoleate	2.5
	
Methyl linolenate	2.8
	
Methyl stearate	0.5
	

3.2 Nitration Product analysis

Infrared analysis and electro-spray ionization mass spectrometry were used to identify and quantify the different chemical compounds produced during the biodiesel nitration.

3.2.1 Infrared analysis

Fig. 2 shows the FTIR spectra of biodiesel and nitrated products at different temperatures. These spectra were obtained after defining the baseline corresponding to the air spectrum with 50 scans. An absorbance difference is noted between 800 and 1700 cm^{-1} . It allows to identify new functional groups present in the nitrated product (Table 2). The value of the nitrated products absorbance depends on the synthesis temperature.

The characteristic ester frequency C=O bonds at 1750 cm^{-1} , alkane frequency C-H bonds between 2900-3000 cm^{-1} and alkene frequency C=C stretch at 1650 cm^{-1} with weak intensity, obviously appear in all spectra. The spectrum of the nitrated product shows the presence of three new peaks at 1363, 1550 and at 1635 cm^{-1} . They respectively indicate the stretching of symmetric NO_2 , that of assymetric NO_2 and the absorption of ONO_2 (fig.3).

The absorption spectrum at 1363 cm^{-1} (fig.3) indicating a symmetric vibration of R-NO_2 for nitrated products, can also be observed in biodiesel but is less intense. This peak in the biodiesel spectrum corresponds to the vibration of CH_2 groups which is supposed to appear at 1370 cm^{-1} .

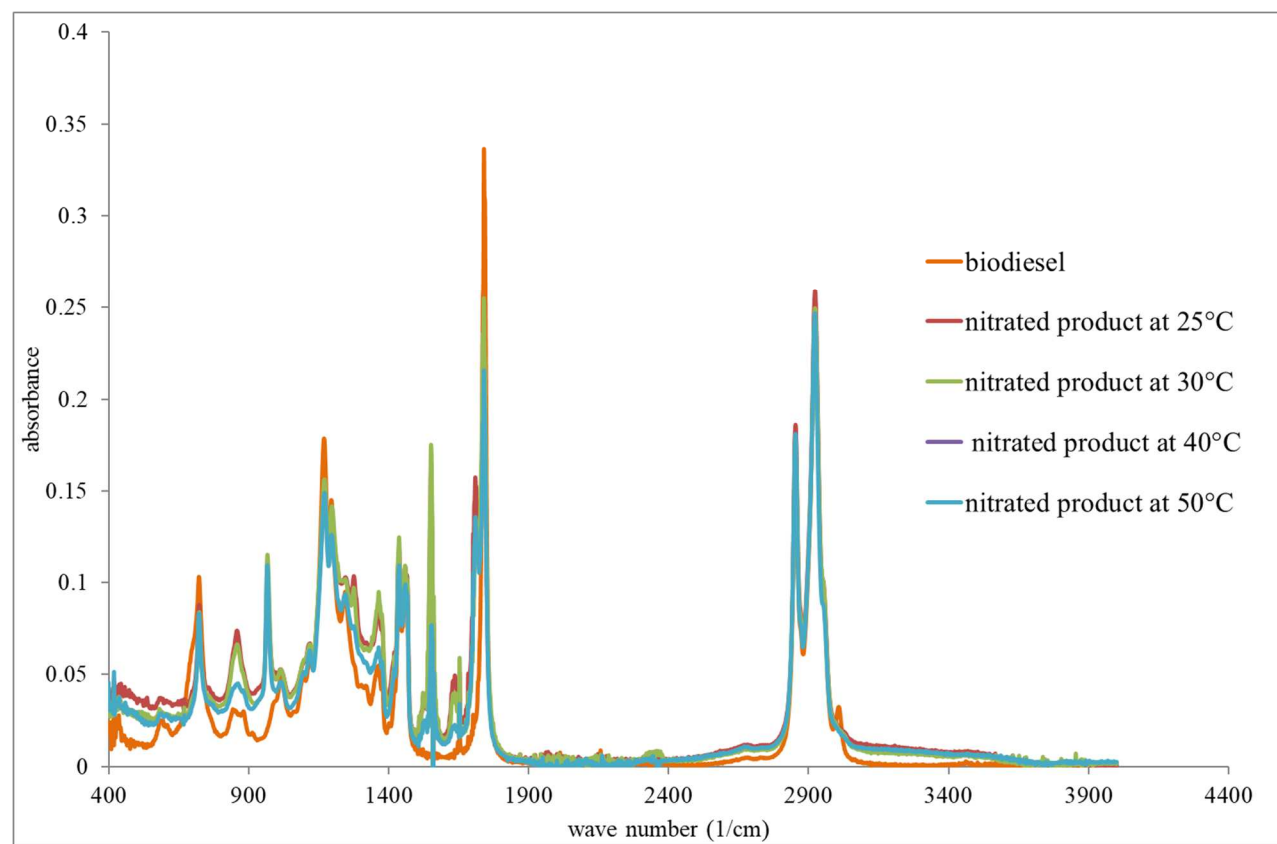


Fig. 2. IR spectra of biodiesel and nitrated products at different temperatures

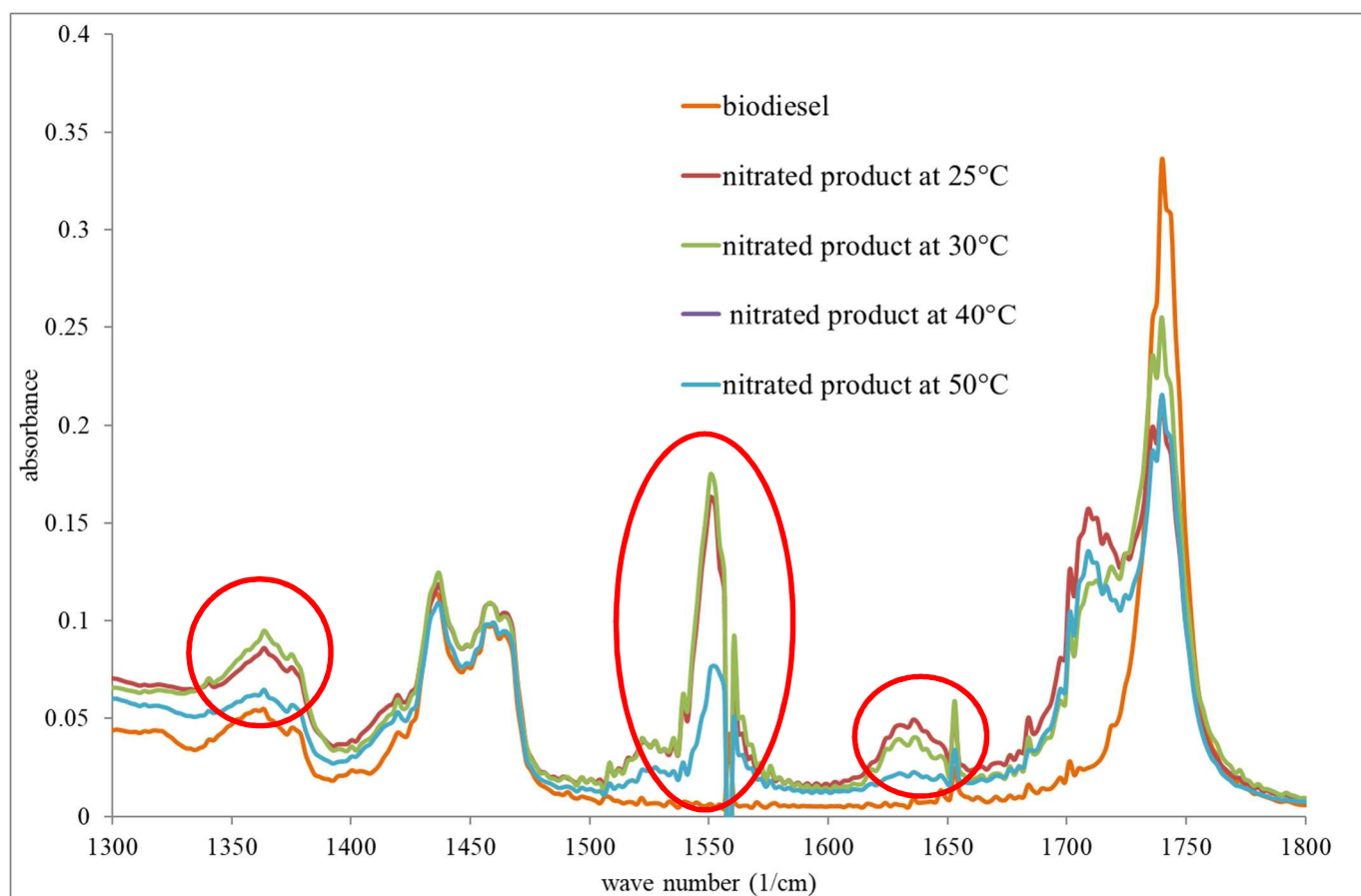


Fig. 3. Zoom on the IR spectra

Table 2: Determination of new functional groups after the reaction

Groups	Theoretical wave number cm^{-1}	Experimental wave number cm^{-1}
RNO ₂ (Asymmetric)	1560-1548	1550
RNO ₂ (Symmetric)	1397-1310	1363
RONO ₂	1640-1620	1635

To complete this IR analysis which only identifies the functional groups, electro spray ionization mass spectrometry was used to identify the synthesized molecules.

3.2.2 Electro spray ionization mass spectrometry

The electro spray ionization mass spectrometry allows to avoid the degradation of the nitrated products during the heating in the chromatography column. The samples (biodiesel and nitro product) were diluted with acetonitrile to a concentration of 20 $\mu\text{g/mL}$, before being introduced into a capillary tube with a flow rate of 15 $\mu\text{L}\cdot\text{min}^{-1}$. Peaks of the spectrum in Fig. 4a correspond to methyl oleate, methyl linolenate and the methyl linoleate. These molecules are in a ionic adduct form $[\text{M} + \text{Na}]^+$ at $m/z = 319$, $m/z = 315$ and $m/z = 317$.

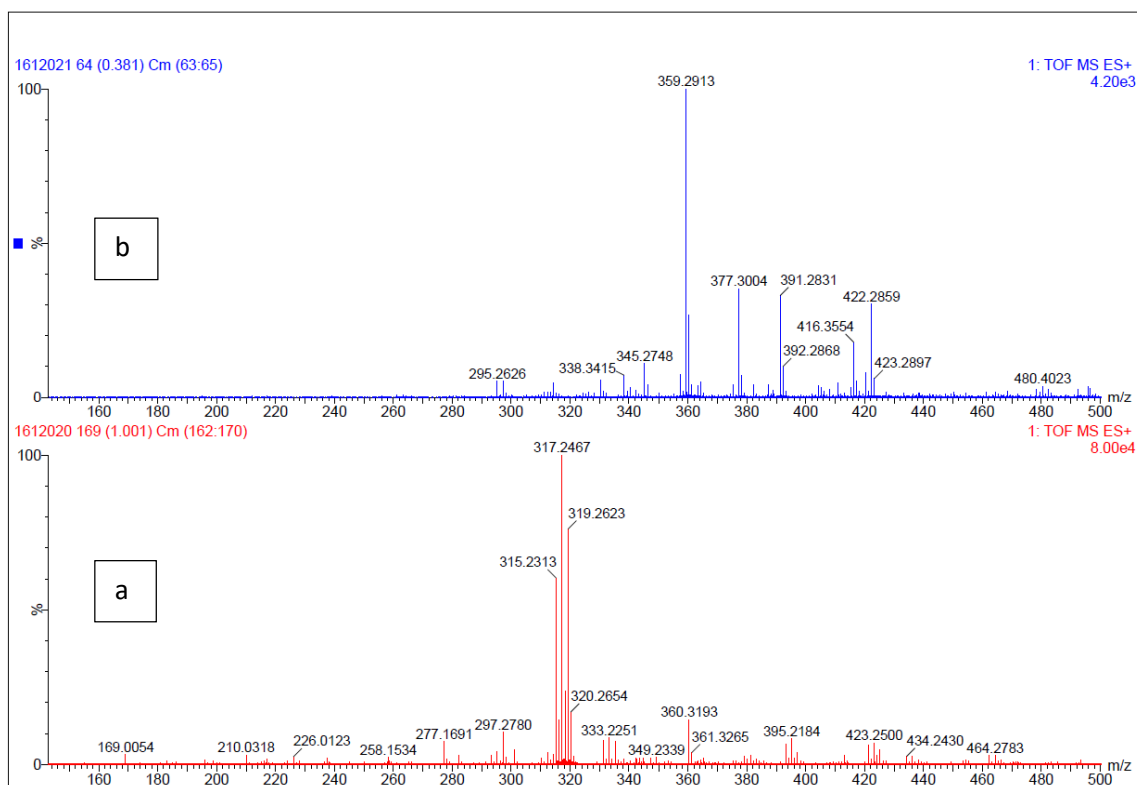


Fig. 4. Biodiesel and nitrated biodiesel mass spectrum

For the nitrated biodiesel (Fig. 4b), intense peaks at m/z 359, 377 and 422 are observed. These peaks correspond to $[M+NH_4]^+$ ion. Table 3 shows the different identified compounds.

Table 3: Molecules after the nitration reaction

Empirical formula	Molar mass	Structural formula
$C_{19}H_{35}NO_4$ A (Methyl-8-nitro oleate)	$341 \text{ g} \cdot \text{mol}^{-1}$	
$C_{19}H_{37}NO_5$ B (Methyl-10-nitrate stearate)	$359 \text{ g} \cdot \text{mol}^{-1}$	
$C_{19}H_{36}N_2O_7$ C (Methyl-10-nitrate-9-nitrostearate)	$404 \text{ g} \cdot \text{mol}^{-1}$	

This study reveals that the nitration reaction can be performed on the carbon atoms carrying the double bond as well as those in the beta position. This result contradicts Abdullah *et al* (2010) [16] work which indicates that during the nitration process the NO₂ or NO₃ groups are attached only on the unsaturated carbon atoms.

Three compounds were identified A (Methyl-8-nitro oleate), B (Methyl-10-nitrate stearate) and C (Methyl-10-nitrate-9-nitrostearate).

3.3 Study of the reaction selectivity

GC-MS and iodine index measurement were used to determine the molar proportion of each compound A, B and C.

3.3.1 Measurement of the conversion rate

The nitration reaction's conversion rate was determined by using a GC-MS with addition of an internal standard (methyl nonadecanoate) according to the 2011 EN14103 standard. Each solution was dissolved in 10 mL of toluene (GC purity $\geq 99.5\%$). 2 μ L of the sample was injected in the column previously heated at 60°C. This column was heated to 200°C with a 10°C/min heating rate then at 5 °C·min⁻¹ to 240°C. Finally, the column was maintained at this temperature during 7 min. The runtime was 30 min. Splitless mode was used.

Results are presented in Table 4

Table 4: Total conversion of the nitration reaction

Temperature (°C)	Conversion rate (%)
25	94.6
30	92.7
40	97.0
50	89.2

Table 4 shows that the reaction conversion rate (the production of all molecules A, B and C) varies with temperature and is maximal at 40 °C. The selectivity of B and C was determined by using the iodine index method.

3.3.2 Determination of the molecules selectivity

The iodine number of oils and fats measures their unsaturation degree. The Wijs method [20], commonly used, requires 30 min absorption time. Sodium thiosulfate solution 0.1M was used as a titration reactant. The measurement of the biodiesel iodine index before and after the nitration reaction allowed to calculate the conversion of unsaturations (the loss of the double bonds). This value was used to determine the proportion of molecules B and C according to the equation 3-1.

$$X = \frac{\text{iodine index}_{t_0} - \text{iodine index}_{t_f}}{\text{iodine index}_{t_0}}$$

3-1

The proportion of A was obtained by making a difference between the conversion rate of the reaction (Table 4) and the unsaturations conversion rate. Results are gathered in Table 5 which shows that at high synthesis temperature, the selectivity of B and C decreases.

Table 5: Determination of the molecule's selectivity

Temperature °C	Total conversion rate (%)	Selectivity of B and C (%)	Selectivity of A (%)
25	94.6	95.2	4.8
30	92.7	68.0	32.0
40	97.0	42.9	57.1
50	89.2	41.6	58.4

The results obtained in this study show that the reaction mechanism of biodiesel nitration (aliphatic chain) is more complex than that of the aromatic compounds. Indeed, three molecules with different selectivity had been identified (Table 5).

During the synthesis at low temperature (below 20°C), the final product is a stable micro emulsion preventing phase separation. This stability may be due to the hydrophilic behavior of the saturated nitrated products (B and C) at low temperatures.

4 Calorimetric study

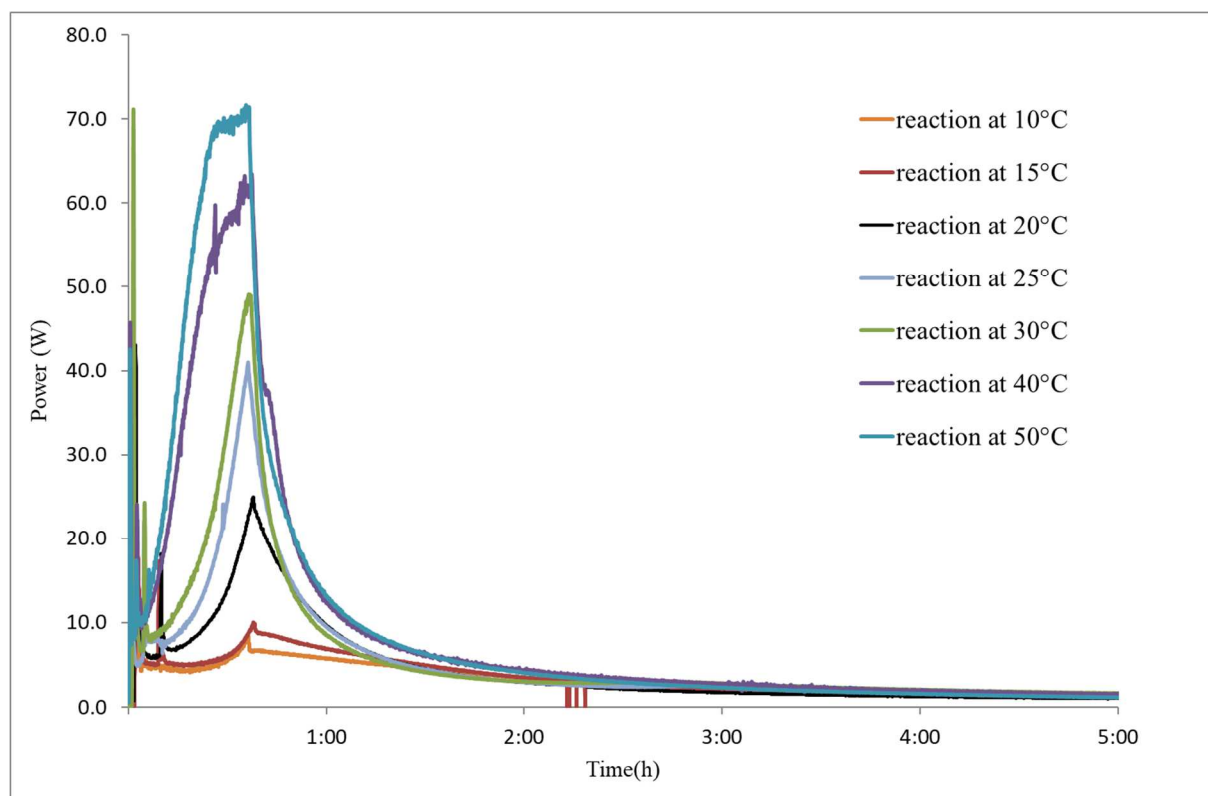
4.1 Determination of the reaction heat

The integration of the experimental power profiles (equation 4-1) obtained according to the conditions presented in section 3, shows that the heat released by the reaction varies with the temperature (Table 6). This change in the thermal behavior has also been observed by Chen et al 2012 [21] in their work about the nitration of iso-octanol but no interpretation has been given. Power profiles (q_r) are shown in Fig.5. Sudden variation of the thermal power with time at the beginning of the reaction corresponds to the nitration of the small amount of the products as Methyl linolenate and Methyl linoleate. Such thermal behavior may present a risk of thermal runaway.

$$Q_R^{\text{Exp}} = \int_{t_0}^t q_r dt$$

4-1

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Fig.5. Power profiles at different temperatures

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Table 6: Heat released by the synthesis reaction at different temperatures

Temperature °C	Heat (kJ)	Conversion rate (%)
25	112.5	94.6
30	106.3	92.8
40	161.9	97.0
50	171.9	89.2

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The total heat released by the reaction (table 6) represents all the thermal effects linked to the products synthesis, to the mixing phenomena and to the possible decomposition in case of unstable compound. In section 3.3.2, a modification of the reaction mechanism according to the synthesis temperature was noticed. In addition to other phenomena mentioned above, the modification of the reaction mechanism is likely to contribute to the change in the total heat released by the reaction.

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Heat related to the mixing phenomena and the decomposition of unstable compounds are presented in sections 4.2 and 4.3.

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4.2 Heat of mixing measurement

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To measure the heat of mixing, the power profile obtained without nitration reaction have to be integrated. The operating conditions were kept identical to those in the synthesis reaction (section 3.1) except for the biodiesel reactant. In fact, to avoid the nitration reaction, the biodiesel was replaced by a molecule close to its main molecule (methyl oleate): methyl palmitate.

The absence of the reaction was confirmed by the palmitate infrared spectrum after the reaction (fig.6: no nitro group was detected). The non-reactivity of the methyl palmitate is due to the absence of unsaturated carbons.

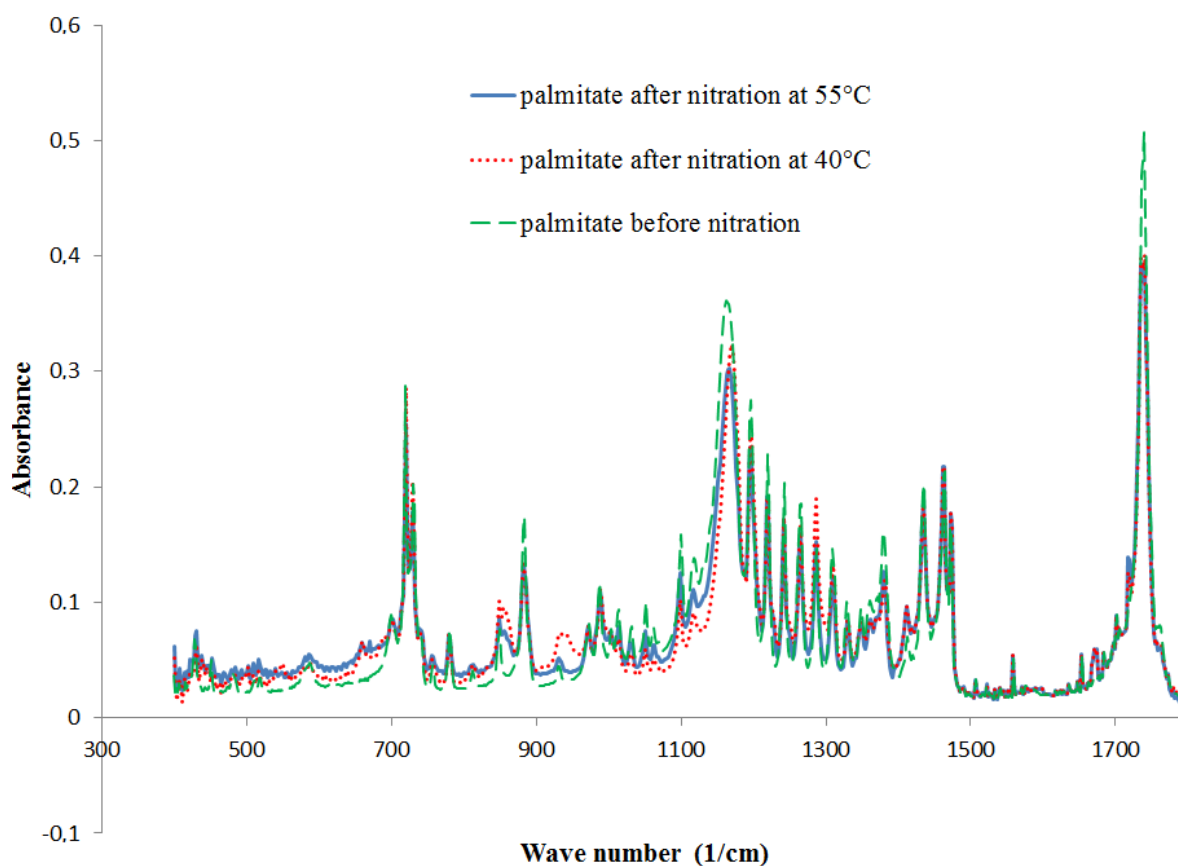


Fig. 6: Methyl palmitate IR spectrum before and after the reaction

The heat of mixing below 40°C could not be measured because the melting point of methyl palmitate is higher than 35°C.

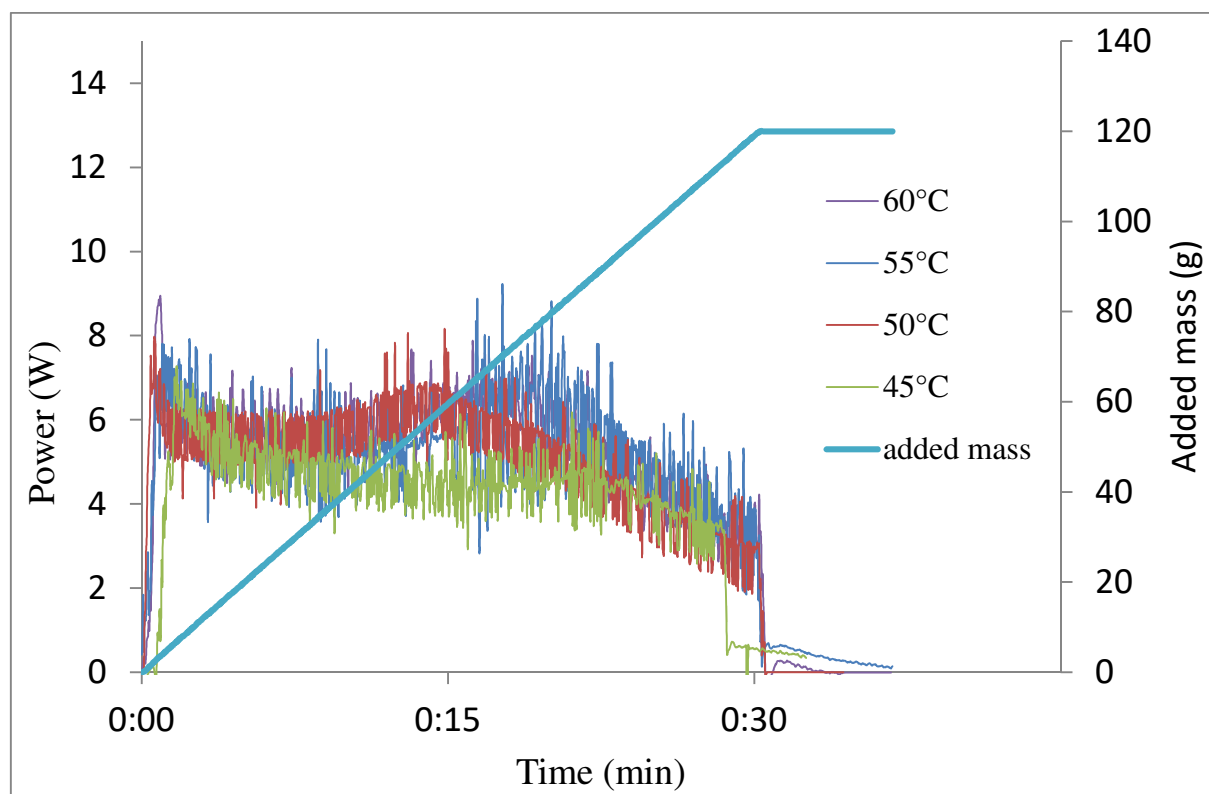


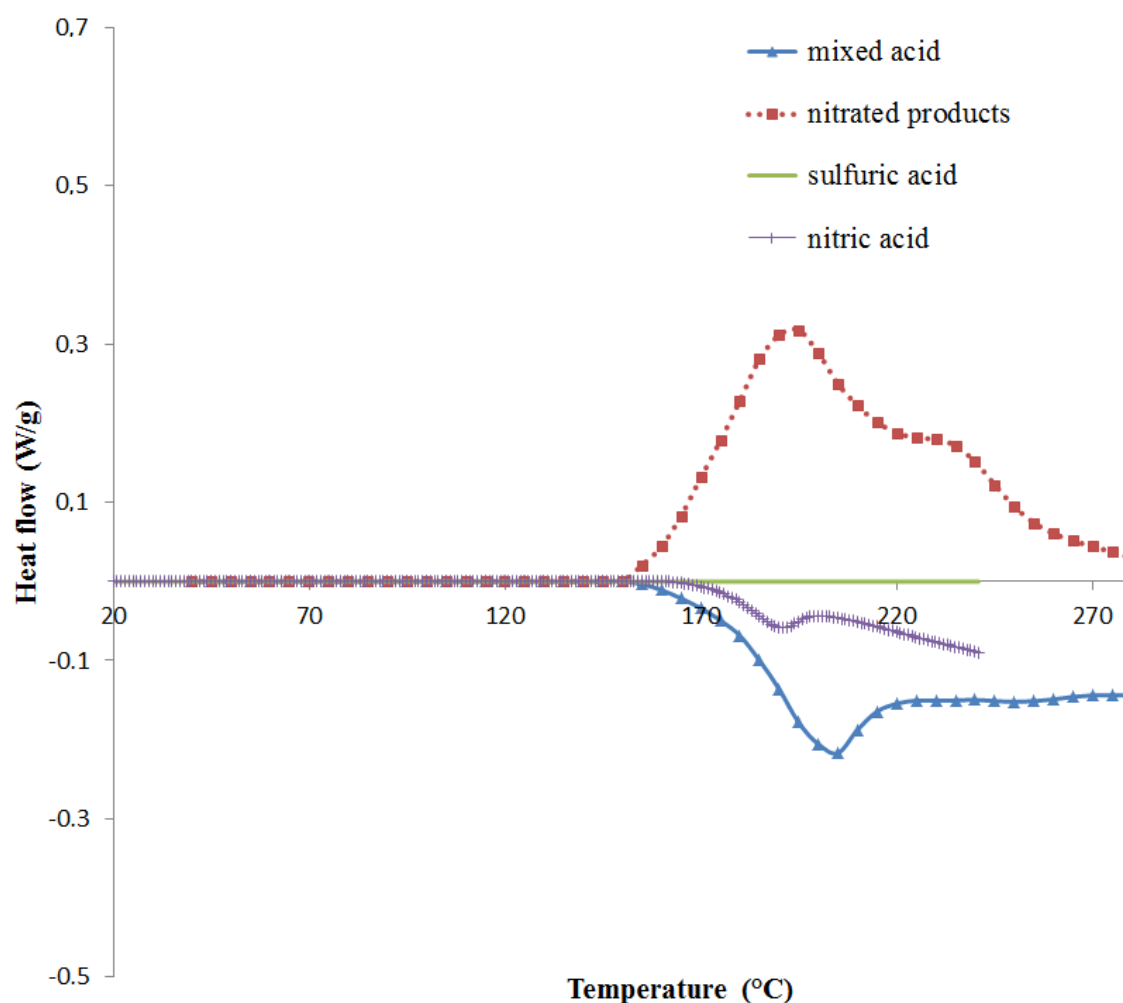
Fig.7. Power profiles obtained with the palmitate

Fig.7. shows that the power profiles are identical regardless of the temperature. The average heat is about 8J. All power profiles return to the baseline at the end of the addition, demonstrating the absence of any chemical transformations.

4.3 Measurement of the decomposition heat

The measurement of the heat released during the decomposition was done in two steps. Pure products: nitrated products, nitric acid, sulfuric acid and mixed acid (sulfo-nitric acid) were analyzed first (fig.8), then samples of mixed acid with different percentages (w/w) of nitrated products (fig.9). These analyses were realized using a DSC in a non-isothermal mode with Gold-plated high-pressure crucibles and a heating rate of $2^{\circ}\text{C}\cdot\text{min}^{-1}$. According to Liu *et al* [22], the advantage of DSC test under non-isothermal condition is its swiftness and high efficiency in a short time.

For pure products (fig.8) no signal of decomposition is observed in our range of synthesis temperature ($<50^{\circ}\text{C}$). The only thermal effects are detected beyond synthesis temperatures. Nitric acid and mixed acid's DSC curves show an endothermic effect at $T_{\text{onset}} = 181.3^{\circ}\text{C}$ which is attributed to the decomposition of the nitric acid [23]. This temperature was determined by the tangent method from zero curvature. Regarding to the nitrated product, it exhibits an exothermic peak at $T_{\text{onset}} = 150.9^{\circ}\text{C}$ which correspond to its decomposition. Its thermal instability was mentioned in other works [9] [24] [21]. The T_{onset} of our additive decomposition is closed to that of fossil nitrated product (EHN) [8].



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Fig. 8. Pure sulfo-nitric acid and pure nitrated product decomposition

264 Fig.9 shows the DSC curves of sulfo-nitric acid mixed with nitrated products. The initial
 265 decomposition temperatures T_{onset} are 48.83°C, 70.39°C and 77.96°C respectively for 50 %,
 266 70% and 90% of mixed acid. Obviously, when the quantity of nitrated products added into the
 267 mixed acid increased, lower onset temperatures are observed. It is also noted that the specific
 268 enthalpy decreases with the amount of nitrated products (table 7). This enthalpy (ΔH) reported
 269 to the total sample mass was determined by integrating the area under the exothermic curve.

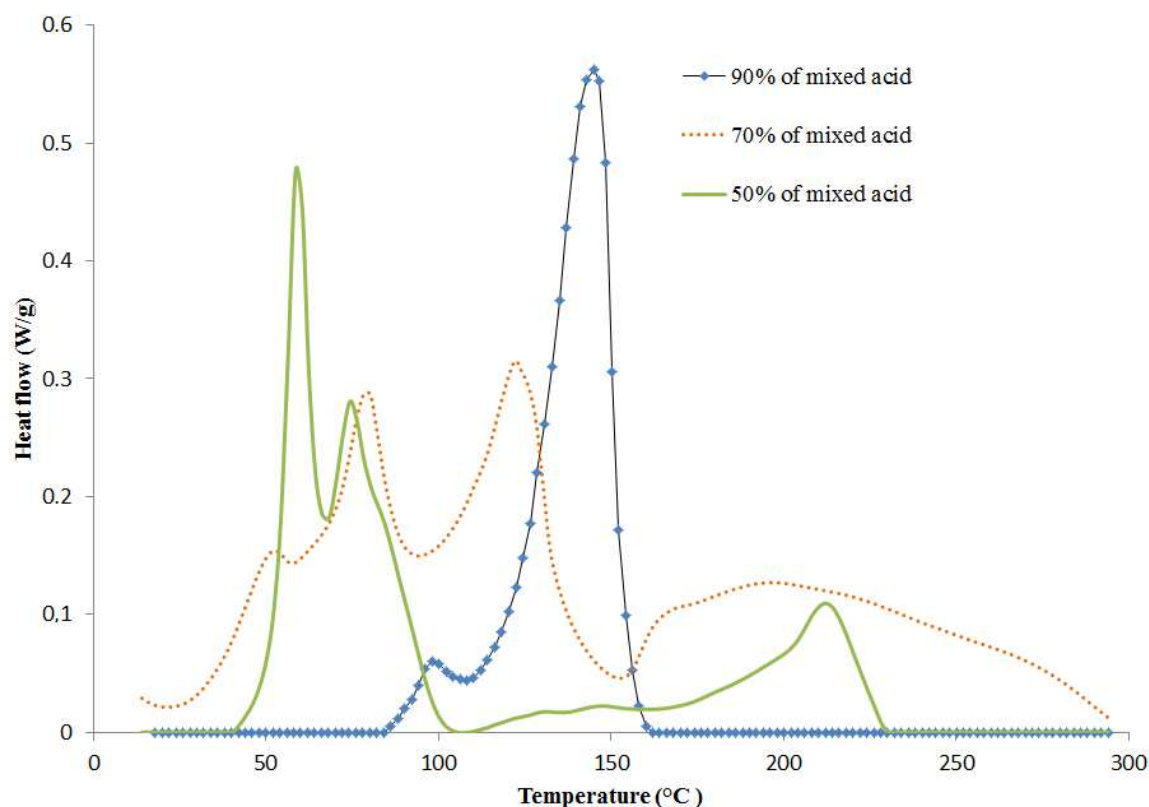


Fig.9. Study of the decomposition mixed sulfo-nitric and nitrated products

This study allows to demonstrate that the decomposition of the sulfo-nitric mixed acid and nitrated products also contributes to the modification of the total heat released during the synthesis reaction (Fig.5).

Table 7: Results of DSC analysis

Component of sample (w/w)	T_{onset} (°C)	ΔH (J/g)
90% of mixed acid and 10% nitrated products	77.96	502.0
70% of mixed acid 30% nitrated products	70.39	474.1
50% of mixed acid 50% nitrated products	48.83	332.1

4.4 Study of the safety parameters

In the light of the strong exothermicity of the nitration reaction and the mixed acid decomposition in the presence of the nitrated products, the determination of the Maximum Temperature of the Synthesis Reaction (*MTSR*) is more than necessary to avoid the possible risk of thermal runaway.

The Maximum Temperature of Synthesis Reaction (*MSTR*) is the temperature reached by the reaction mixture if the energy potential of the main reactions is released under adiabatic conditions [25].

This decomposition releases an excess of energy causing a thermal runaway. To evaluate this temperature, it is necessary to determine the ΔT_{ad} (the temperature variation in adiabatic mode) according to equation 4-2.

$$\Delta T_{ad} = \frac{Q_R^{exp}}{C_p Mr X'_r} \quad 4-2$$

with C_p the heat capacity of reaction mixture obtained with reaction calorimeter, Mr the mass of the reaction mixture and X'_r the full conversion of the biodiesel.

The calculation of the $MTSR$ was done in semi-batch mode according to equation 4-3 [26] [25]. The results are given in Table 8. They show a considerable increase in $MTSR$ from an isothermal of 40 °C. This can be explained by the fact that the value of the adiabatic temperature increase ΔT_{ad} used for the calculation of $MTSR$, considers the enthalpy of the nitration reaction in addition to the decomposition enthalpy.

$$MTSR = T_P + \Delta T_{ad} \cdot X_{ac, max} \quad 4-3$$

with $X_{ac, max}$ the maximum accumulation of the unreacted reactant and T_P the synthesis temperature.

In our case, the nitric acid is in stoichiometric excess over biodiesel. Thus $X_{ac, max}$ is obtained at the end of the addition.

Table 8: Safety parameters of nitration reaction

Temperature (°C)	Conversion (%)	C_p (J·g ⁻¹ ·°C ⁻¹)	ΔT_{ad} (°C)	$X_{ac, max}$ (%)	$MTSR$ (°C)
25	94.6	2.1	194.4	30.3	83.8
30	92.8	2.0	194.8	36.5	101.2
40	97.0	2.2	262.8	49.5	171.1
50	89.2	2.1	313.6	50.5	208.5

If we compare results in table 7 with those in table 8, it appears that the lowest $MTSR$ (83.8°C) is higher than the maximum T_{onset} obtained in decomposition study (77.96°C). In case of loss of temperature control, this means that the decomposition reaction would be triggered before completion of the synthesis reaction, which would further lead to very severe consequences. According to Stoessel's criticality index used for the risk assessment of a chemical reaction [27], this implies that the runaway is too fast for a safety barrier to be efficient. These results correspond to a Stoessel's criticality class of 5 if the nitration reaction conducted in these operated conditions.

5 Measurement of the bio-additive cetane number (index)

The cetane number is the measurement of the diesel fuel ignition performance. It is obtained by making some comparison with reference fuels in a standardized test. Higher cetane number indicates that the ignition properties of the fuel are better [28]. This index is obtained according to ASTM D 613. The equipment used was a Cooperative Fuel Research (CFR) engine. A standard diesel of cetane number 50 was used to prepare two samples of 1% and 5% concentration in bio-additive. For each mixture, the cetane number was measured at two synthesis temperatures 25 and 40 °C. The results of the cetane number analysis are listed in Table 9. They show that the bio-additive synthesized in this study allows to increase the cetane number of the reference diesel. A 5% addition of the bio-additive to the reference diesel improves the cetane number by 3 points.

Table 9: Cetane number with the CFR engine

Synthesis temperature (°C)	CN fuel		
	CN fuel	CN fuel +1% additive	+ 5% additive
25	50.0	50.9	52.9
40	50.0	50.9	53.2

Canoira *et al* 2012 [13] obtained a 5 points increase in the fuel cetane number by mixing their nitrated biodiesel to fossil diesel in a concentration of 1000 mg.L⁻¹. With our bio-additive a 5% addition (concentration of 49g.L⁻¹) to the reference diesel improves the cetane number by 3 points. It seems clear that our bio-additive is much less efficient than Canoira *et al* one. It may be due to the fact that Canoira *et al* used a biodiesel containing 33.0 %, 54.20% and 16% of methyl linoleate while ours contains only 2.5%. According to Abdullah *et al* 2010 [16], during the nitration process of biodiesel, NO₃ or NO₂ groups are grafted to the double bonds of carbon atoms. Based on this statement, biodiesel containing more double bonds, once nitrated, tend to be more energetic than others. That could explain the big different between these 2 results.

However, the difference between our additive and the EHN is not so high. Indeed a 2.5% and a 5% addition of EHN on BN20 (diesel with 20% of methyl ester) leads respectively to an increase in cetane number of 2.5 and 6.5 points [29].

6 Conclusion

The results of chemical analysis of the nitrated products showed the presence of 3 different compounds (methyl-8-nitro oleate, methyl-10-nitrate stearate and methyl-10-nitrate-9-nitrostearate), whose selectivity varies according to the synthesis temperature. Some of these compounds, particularly the methyl-8-nitro oleate and the methyl-10-nitrate-9-nitrostearate, were also identified by Canoira *et al.* [13] and Malins *et al.* [30].

The heat released by the chemical transformation obtained with the reaction calorimeter RC1-*RTCal* varies with the synthesis temperature. This difference in the thermal behavior is due to the complexity of the reaction mechanism as well as the instability of the nitrated products and sulfo-nitric acid mixture. The study of the thermal stability shows that the T_{onset} of the decomposition is around 40°C. Thus, at high synthesis temperature (beyond the T_{onset}), the heat measured by the RC1 corresponds to the sum of the heat released by the nitration reaction and that of the mixture decomposition. This thermal and chemical behavior shows the complexity of the aliphatic compound nitration compared to the aromatic compounds one.

The modification of thermal behavior according to the synthesis temperature increases the risk of thermal runaway. The Maximum Temperature of the Synthesis Reaction (*MTSR*) obtained is higher than the sulfo-nitric acid temperature of decomposition, which leads to important risks of thermal runaway. To avoid thermal runaway while having a high conversion rate, the synthesis temperature, the flow rate of sulfo-nitric acid as well as the temperature control of the cooling fluid are the main parameters on which we can lean on.

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