23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

THERMOCHEMISTRY AND THEORICAL COMPARISON OF THE COMBUSTION OF TYRE PYROLYSIS OIL (TPO) AND DIESEL

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Abstract. *On the current world industrial scenario, the consumption of fossil fuels has shown to be a great concern, since it causes considerable damages to the environment. Taking these problems into consideration, all over the world, a lot of tecnologies for cleaner fuels utilization instead of the current ones are beeing developed. Another environmental impact that has also been noted is the great number of unusable waste tyres. With the growing number of vehicles around the world, a new concern arises; finding a correct destiny to waste tires. Considering these two factors, the purpose of this work is to analyse an alternative fuel oil provided from the pyrolysis of waste tyres, focusing on a thermochemichal comparison between this tyre pyrolytic oil (TPO) and diesel. The objective of this comparison is to find similar characteristics between the TPO and diesel, and verify if it is possible to mix both oils to create a more sustainable fuel. The methodology used in this work is divided firstly into a theorical analysis of liquid fuels, and theormodynamics of combustion, and secondly into an experimental analysis of atomization and calculation and comparison of physical chemical properties of TPO and diesel. (CNPq Proc. N°442050/2014-3)*

Keywords: *tyre pyrolytic oil (TPO), atomization, combustion, diesel, waste tyres.*

1. INTRODUCTION

A fuel represents a material that when in contact with an oxidant it can be altered to release energy in a controlled form. The release of energy presumes the existence of an energy transfer mechanism. According to thermodynamics, the energy transfer mechanism between a system and its surroundings must be by heat or work. In the combustion of fuels, energy is released in the form of heat. The majority of fuels are used in direct combustion processes, but they can also be used in thermochemical transformations processes such as pyrolysis, gasification or carbonization. Fuels can be solid, liquid or gaseous, but the combustion process and the geometry of the combustion chamber are altered for each of these phases.

Most Liquid fuels are derived from petroleum (gasoline, diesel, kerosene) but there are some which are not, for example, ethanol (ethyl alcohol) and vegetable oils, both are considered clean and renewable fuels. In Brazil there is ample production of ethanol from biomass plantations, mainly sugar cane. Usually these renewable fuels are blended with fossil fuels to reduce dependence on fossil sources and also reduce the environmental impact. Mixing fossil fuels with biofuels is a good way to transition to a sustainable energy economy. In Brazil, the federal government passed a law increasing the percentage of biodiesel in diesel as well as ethanol percentage in gasoline. The biodiesel mixture in diesel was 6 % from July 2014 and to 7% from November 2014. The mix of ethanol in gasoline is undergoing tests to move from 25 % to 27.5 % in 2014. [Folha de São Paulo, 2014]

It is a known fact that the dependence on fossil fuels has generated a negative impact on the environment, with the emissions of pollutant such as SO_2, NO_x, CO_2, etc. Another environmental impact that runs parallel to this is the existence of a great amount of waste that is discarded all over the world. The waste amount in the European Union sums up to 1.43 billons of tons per year [Martínez, 2013]. Even though a lot of this garbage does not biodegrade, they are disposed of improperly due to a lack of specific regulations and/or because the recycling of these materials is not economically attractive. A possible solution to the dependence on fossil fuels, as well as the reduction of waste dumping in the environment is the use of this waste to generate energy.

The tyre production in Brazil has increased from 57.3 million tyres in 2007 to 68.8 million in 2013 [ANIP, 2013], which causes an increased necessity to dispose of unusable tyres without simply throwing them in the environment, that's why, since 1999 in Brazil, the government agencies started to create laws in which both the producers and the sellers become responsible for all tyres produced in national territory, in attempt to reduce the pollution and waste caused by piles of tyres in landfills and other deposits. Besides this management of the waste tyre, there are other ways to relocate these unusable tyres, such as the asphalt and concrete industries, and find a use for them as a biofuel.

Tyre pyrolytic oil (TPO) is a biofuel obtained by means of pyrolysis of the waste tyre. Pyrolysis is a thermochemical process that degrades the material, without the presence of oxygen. Its main products are oil, gas and char. The greatest

product obtained is the liquid fraction, although its amounts can vary significantly, because there are many parameters to be analysed in the production of TPO. Among these parameters is the type of pyrolysis, which can be fast, slow or catalytic, as well as the type of reactor used for the process. The TPO can be used in the same way as bio-oils: by mixing them with diesel, which is the fuel that has the most similar proprieties, as it can be seen in table (1).

Table 1. Comparison between TPO characteristics and ordinary Diesel [Rofiqul Islam, 2008]

Analyses (wt%)	TPO	Diesel
C	85.86	84-87
H	9.15	12.80 - 15.70
N	0.65	65-3000ppm
S	1.25	1100-7000ppm
Ashes	0.22	0
O	2.87	0
Density[kg/m³]	957	820-860
Viscosity [cSt]	4.75	2.0-4.5
Flash point [ºC]	<32	>55

2. THERMODYNAMIC PROCESS: COMBUSTION

2.1 Stoichiometric Combustion

When a chemical reaction occurs, the bonds between the molecules of the reagents are broken, and the atoms and electrons rearrange to form products. In combustion, the rapid oxidation of the fuel results in release of energy while the combustion products are formed, this kind of reaction with release of energy is called exothermic reaction. Generally, the combustion reaction is expressed as equation (1):

$$\text{Fuel+ Oxidizer} \rightarrow \text{Products + Energy} \quad (1)$$

The fuel and oxidant are called reactants. The most commonly used oxidant is atmospheric air, which is composed of 20.95% O_2 and 78.08 % N_2 and 0.97 % of other gases, but is usually considered to be 21 % O_2 , 79% N_2 for balancing calculations. Therefore, it is used: (1 O_2 + 3.76 N_2), i.e. for each mole of O_2 it is used 3.76 moles of N_2.

The combustion is said to be theoretical or stoichiometric when in the combustion chamber all elements are completely oxidized, i.e. all the carbon in the fuel is converted to carbon dioxide (CO_2), all hydrogen is converted to water (H_2O), all sulfur is converted into sulfur dioxide (SO_2), and all nitrogen present in the reactant is converted into gaseous nitrogen (N_2). Sulfur is usually not a big energy creator, but is a major cause of pollution and corrosion.

A reaction example where all the elements are oxidized is the complete combustion reaction of butane gas, which burns out, for example, when a common lighter is lit, as shows eq. (2).

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O \quad (2)$$

The coefficients in front of the molecules are called stoichiometric coefficients and are calculated by balancing atoms on each side of the equation. It is noted that the balancing is done with the atoms because the substances in the reagent are not the same substances in the product.

Most fuels have very complex chemical formula because they have different components, which is mainly the case of oil fuels. To estimate the amount of energy released by the combustion of a fuel, it is essential to have knowledge of the chemical formulation of the fuel. For example, the balanced reaction for fuels with complex formulation is shown on Eq. (3) using TPO with compositions from *Williams, 1998* (all calculations will be made with this composition, unless stated otherwise). Table (2) shows different compositions of TPO for various references including Williams' composition.

Table 2. Composition of TPO for various references

Composition (wt%)	Williams *et al*, 1998	Li *et al*, 2004	Banar *et al*, 2012	Rofiqul Islam, 2008
C	88.13	84.26	79.61	85.86
H_2	9.41	10.39	10.04	9.15
N_2	0.0451	0.42	0.94	0.65
SO_2	1.5	1.54	0.11	1.25
O_2	0.5	3.39	9.3	2.87

$$(7.344C + 4.705H_2 + 0.016N_2 + 0.047S + 0.016O_2) + z(O_2 + 3.76N_2) \rightarrow xCO_2 + yH_2O + wSO_2 + (z3.76 + 0.016)N_2 \quad (3)$$

$x = 88.13/12 \rightarrow x = 7.344$ moles of CO_2/mole of fuel;
$2y = 2(9.41/2) \rightarrow y = 4.705$ moles of H_2O/mole of fuel;
$2x + y + 2w = 2(0.5/32) + 2z \rightarrow z = 9.728$moles of air/mole of fuel;
$2w = 1.5/32 \rightarrow w = 0.047$ moles of SO_2/mole of fuel;

Eq. (4) shows the balanced reaction:

$$(7.344C + 4.705H_2 + 0.016N_2 + 0.047S + 0.016O_2) + 9.728(O_2 + 3.76N_2) \rightarrow 7.344CO_2 + 4.705H_2O + 0.047SO_2 + (36.58+0.016)N_2 \quad (4)$$

2.22 Air excess (α) and stoichiometric air

The relationship between the amount of air and fuel used in the reaction is extremely important for the thermochemistry of fuel burning, considering that the formation of combustion products is directly affected by the air/fuel ratio. For solid and liquid fuels the relationship is between the masses, for gaseous fuels the relationship is calculated between the volumes involved.

An exact amount of air is required to provide sufficient oxygen for complete combustion of the fuel; this minimum amount is referred to as stoichiometric air or theoretical air. When stoichiometric conditions are not met, i.e., if the air supplied is less than the necessary, the combustion is incomplete. The effectiveness of the fuel and the engine output decreases in incomplete combustion conditions, in addition, the main product of incomplete combustion is carbon monoxide, which is an asphyxiating chemical, for those reasons is undesirable to have incomplete combustion.

In reality, to ensure complete combustion and avoid the formation of CO, it is supplied in the combustion chamber an amount of air greater than the stoichiometric, i.e. there is an excess (α) of air in the combustion reaction. If there is excess air in the reaction, there will be O_2 presence in the combustion products, so we can determine the excess air in the combustion by calculating the amount of O_2 in the products. The presence of O_2 in the combustion products of the TPO reaction with excess air can be observed in eq. (5):

$$(7.344C + 4.705H_2 + 0.016N_2 + 0,047S + 0.016O_2) + \alpha 9.728(O_2 + 3.76N_2) \rightarrow 7.344CO_2 + 4.705H_2O + 0.047SO_2 + (\alpha 36.58+0.016)N_2 + (\alpha-1)O_2 \quad (5)$$

There are three parameters used to determine the amount of air used in a combustion reaction for a given fuel; the air/fuel ratio (AFR), its reciprocal fuel/air ratio (FAR), and the equivalence ratio (Φ). One can calculate the air/fuel ratio of TPO on mass basis by eq. (6):

$$(AFR) = \frac{(9.728 \cdot 32)+(36.58 \cdot 28)}{100\text{g of fuel}} = 13.35 \frac{\text{g of air}}{\text{g of fuel}} \quad (6)$$

The criteria established for air-fuel mixture quality is; fuel-lean, stoichiometric, and fuel-rich. Stoichiometric is the ideal perfect proportion of air-fuel for complete combustion. Fuel-lean is when the AFR has a reduced amount of fuel than stoichiometric. On the other hand, fuel-rich is an AFR with a larger amount of fuel than stoichiometric. A relationship that determines whether a mixture of air and fuel is rich, lean or stoichiometric is the equivalence ratio (Φ). This is a relationship between stoichiometric AFR and the real AFR, both in mass, as shown in eq. (7):

$$\Phi = \frac{(\text{AFR})_{\text{stoich}}}{(\text{AFR})_{\text{real}}} \quad (7)$$

$\Phi < 1 \rightarrow$ Combustion is fuel-lean
$\Phi = 1 \rightarrow$ Stoichiometric combustion

$\Phi > 1$ → Combustion is fuel-rich

Considering the TPO reaction with 10% of excess air, as shown in eq. (8):

$$(7.344C + 4.705H_2 + 0.016N_2 + 0.047S + 0.016O_2) + 10.701(O_2 + 3.76N_2) \rightarrow 7.344CO_2 + 4.705H_2O + 0.047SO_2 + (1.1*36.58+0.016)N_2 + (1.1-1)O_2 \quad (8)$$

Eq. (9) demonstrates the calculation for the equivalence ratio:

$$\Phi = \frac{(\text{AFR})_{\text{stoich}}}{(\text{AFR})_{\text{real}}} = \frac{13.35}{14.69} = 0.909 \quad (9)$$

In practice it is provided an air excess around 1 to 2% for gaseous fuels, from 5 to 10% for liquid fuels and for solid fuels excess air can reach up to 25 %. [Carvalho, 2007]

3. EMISSIONS

The setting of parameters for emissions of gaseous components and particulate materials by stationary sources (industries, power plants) began to be made by the CONAMA resolution which sets up the *Programa Nacional de Controle da Poluição do ar* (PRONAR) and began to be made for movable sources (motor vehicles) through the *Programa de Controle da Poluição do ar por Veículos automotores* (PRONCOVE). Those resolutions set up specific emission limits for each source or fuel.

3.1 CO_2 Emissions

The analysis and measures of CO_2 emissions (which is considered one of the key agents of the greenhouse effect therefore one of the main agents of global warming) are required in fuel combustions.

One can analyze the amount of CO_2 formed, for example, for the complete combustion reaction of TPO previously exemplified in eq. (4). As the CO_2 molar mass is 44g, which gives: 7.344 * 44g = 323.1g of CO_2 per 100g fuel. Since the specific mass of TPO is 0,91ton/m³ [Williams et al, 1998], which gives: 323.1 tons of CO_2 per 110m^3 of TPO. i.e.: 2.94 tons of CO_2 per m^3 of TPO.

For comparison, one can analyze the formation of CO_2 by the combustion of diesel ($C_{12}H_{26}$) exemplified in eq. (10).

$$1C_{12}H_{26} + 18.5(O_2 + 3{,}76N_2) \rightarrow 12CO_2 + 13H_2O + 69.6N_2 \quad (10)$$

The CO_2 molar mass is 44g. Therefore: 12*44g = 528g of CO_2 per 1 mole of fuel. The diesel's molar mass is 170 g/mole. Since the specific mass for diesel is 853kg/l, which gives: 0.1993 liters of diesel per mole of diesel. Eq. (11) shows the calculation of the amount of CO_2 formed by cubic meter of diesel.

$$\frac{528 \text{ g of } CO_2/\text{mole}}{0.1993 \text{ l/mole}} \cdot \frac{1000\text{l}}{1\text{m}^3} = 2.64 \frac{\text{ton of } CO_2}{\text{m}^3} \quad (11)$$

Thus, it can be considered that a car runs 60,000 kilometers a year and has a 25 % mixture of TPO in diesel. If this car runs on average 8 km per liter of fuel, one can calculate its annual rate of CO_2 emissions, shown in eq. (12) and eq. (13):

$$\frac{60.000km/year}{8km/l\ fuel} = 7.500 \frac{l\ fuel}{year} * \frac{1m^3}{1000l} = 7.5 \frac{m^3 fuel}{year} \quad (12)$$

As the fuel is é 25% TPO e 75% diesel:

$$(0.25*2.94 + 0.75*2.64) = 2.72t\ of\ CO_2\ per\ m^3 of\ fuel \quad (13)$$

Its annual rate is as shows eq. (14):

$$7.5 \frac{\text{m}^3\text{fuel}}{\text{year}} * 2.72 \frac{\text{ton of } CO_2}{\text{m}^3 \text{ fuel}} = 20.4 \text{ ton of } CO_2/\text{year} \quad (14)$$

3.2 SO_2 EMISSIONS

SO_2 is a toxic gas which is released by burning sulfur-containing materials; it can be significantly detrimental to human health. It is considered an atmosphere pollutant and a major agent of acid rain. One can analyze, for example, the formation of SO_2 in the combustion of TPO, considering eq. (4). The molar mass of SO_2 is 64g, therefore it gives: 64g*0.047 = 3.01g of SO_2 per 100g of fuel. Since the specific mass of TPO is 0,91ton/m^3 [Williams et al, 1998], it results in: 3.01ton of SO_2 per 110m^3 of TPO. That is, 0.027 tons of SO_2 per m^3 of TPO.

4. HIGHER AND LOWER HEATING VALUE (HHV, LHV)

The heating value or calorific value is the amount of heat released by a substance in combustion, per its mass quantity. In the international system (IS), its unit is in kJ/kg. It can be classified into two types: the High Heating Value (HHV), which is the combustion heat considering that all the water in the product is condensed, and the Lower Heating Value (LHV), which is obtained by assuming that all the water is presented as vapor between products. Given that, in the calculations, the most widely used is the LHV and it is very common to find the heating value per mass unit. The relationship between HHV and LHV is represented in eq. (15):

$$\text{HHV [kJ/kg]} = \text{LHV-2440(9H + u)} \tag{15}$$

Where:
u = moisture content of the fuel [kg of water/kg of fuel]
H= hydrogen content of the fuel [kg/kg in dry mass basis]

5. HEAT OF COMBUSTION AND HEAT OF FORMATION

The difference between the enthalpy of formation of the reactants and the enthalpy of formation of the products is the heat of combustion, also known as the heating value of the fuel. This parameter must also be specified at a given temperature, in this study, 25°C. Thus the calculation of the heat of combustion for the TPO is exemplified in eq. (16):

$$\Delta H_C = \overline{h}_{f,r} - \overline{h}_{f,p} = \overline{h}_{f,TPO} - (\overline{h}_{f,CO2} + \overline{h}_{f,SO2} + \overline{h}_{f,H2O}) \tag{16}$$

The enthalpy of formation is the energy released or absorbed when a compound is formed by its chemical elements, being that both the compound and elements are in the reference condition [Carvalho, 2007]. It's not necessary to consider the ash for the calculation of the enthalpy of formation for TPO because it does not react with oxygen. Thus, the enthalpy of formation for TPO is calculated using eq. (16) and represented on eq. (17):

$$LHV_{TPO} = h_{f,TPO} - (7{,}344\ h_{f,CO2} + 4{,}705\ h_{f,H20} + 0{,}047 h_{f,SO2}) \tag{17}$$

Thus, using the LHV of 42,000 kJ/kg [Williams et al, 1998] and in similar form to the previous balanced chemical reaction (considering 100g of fuel) and along with literature values for $h_{f,CO2}$ (-393520 kJ/kmol), $h_{f,H2O,v}$ (-241820 kJ/kmol), and $h_{f,SO2}$ (-296940 kJ/kmol). The value for the enthalpy of formation for TPO is 158246.1 kJ/kmol. Fig. (1) shows the behaviour of $h_{f,TPO}$ in respect to LHV values found in literature for various TPO compositions.

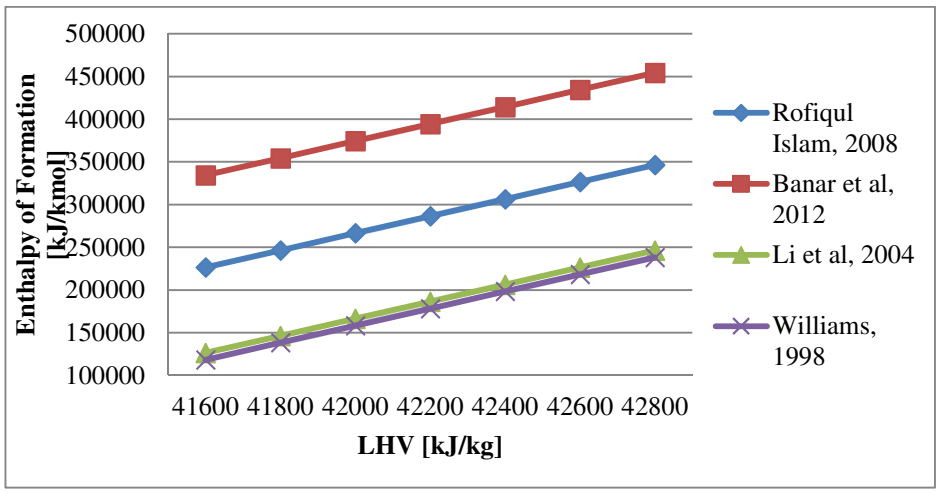

Figure 1. Correlation between the fuel enthalpy of formation and LHV.

6. ADIABATIC FLAME TEMPERATURE

The adiabatic flame temperature (T_{ad}) is the highest temperature that can be obtained for the combustion products, occurring when there is no heat exchange out of the system, during the combustion process.

6.1 Adiabatic flame temperature using specific heat:

For this method of calculation of T_{ad} it is necessary to know the specific heat at constant pressure (C_p), of the gas mixture that is the combustion products. Since the specific heat varies with temperature, and also since it is normally formed by a gas mixture, it is necessary to find the specific heat for each of the combustion products, along with its corresponding number of moles. Of these variables, it is formulated the equation necessary for the calculation of T_{ad}, determined by eq. (18):

$$\Delta H_C = \int_{T_I}^{T_F} \sum_i n_i c_{p,i} dT \tag{18}$$

Where:
ΔH_c = Heat of combustion of the reactant element
n = Number of moles of the element in stoichiometric reaction
c_p = Specific heat of the element

Furthermore, the excess air (α) needs to be considered in cases where it occurs. In these situations, the value of α must be introduced in the equation, in order to correctly perform the calculation. The equation for the calculation of T_{ad} for the TPO is represented in eq. (19):

$$\Delta h_{c,TPO} = \int_{298}^{TF} (c_p CO_2 + c_p H_2O + c_p SO_2 + c_p N_2 + c_p O_2) dT \tag{19}$$

Table (3) displays the values for the coefficients to perform the calculation of the specific heats of certain substances using eq. (20) [CENGEL, 2007], where T is in Kelvin:

$$Cp = a + b\,T + c\,T^2 + d\,T^3 \tag{20}$$

Table 3: Coefficients to calculate specific heat

SUBSTANCE	a	b	c	d
CO_2	22.26	5,981 e-2	-3,501 e-5	7,469 e-9
H_2O	32.24	0,1929 e-2	1,055 e-5	-3,595 e-9
N_2	28.9	-0.001571	0,8081 e-5	-2,873 e-9
SO_2	25.78	5,795 e-2	-3,812 e-5	8,612 e-9

Using Eq (20) along with the coefficient values on table (3), it is possible to find the value of T_{ad} for the combustion of TPO as shown in eq. (21):

$$LHV = 7.344 \int_{298}^{TF} 22.26 + 5.981 \cdot 10^{-2} T - 3.501 \cdot 10^{-5} T^2 + 7.469 \cdot 10^{-9} T^3 9 + 4.705 \int_{298}^{TF} 32.24 + 0.1929 \cdot 10^{-2} T + 1.055 \cdot 10^{-5} T^2 - 3.595 \cdot 10^{-9} T^3 + \alpha 36.58 \int_{298}^{TF} 28.9 - 0.1571 \cdot 10^{-2} T + 0.8081 \cdot 10^{-5} T^2 - 2.873 \cdot 10^{-9} T^3 + 0.047 \int_{298}^{TF} 25.78 + 5.795 \cdot 10^{-2} T - 3.812 \cdot 10^{-5} T^2 + 8.612 \cdot 10^{-9} \tag{21}$$

Solving this equation and establishing a value for α, for example α =1, thus: T_{ad} = 2590K. Figure (2) shows the correlation between T_{ad} and LHV for various compositions of TPO found in literature using the specific heat method for calculation. For Diesel with the following composition: 85% C, 14% H_2, 0.2% N_2, 0.4% SO_2 [Rofiqul Islam, 2008] and calorific value of 42.11MJ/kg [Pérez, 2007], and α =1, T_{ad} = 2381.1K.

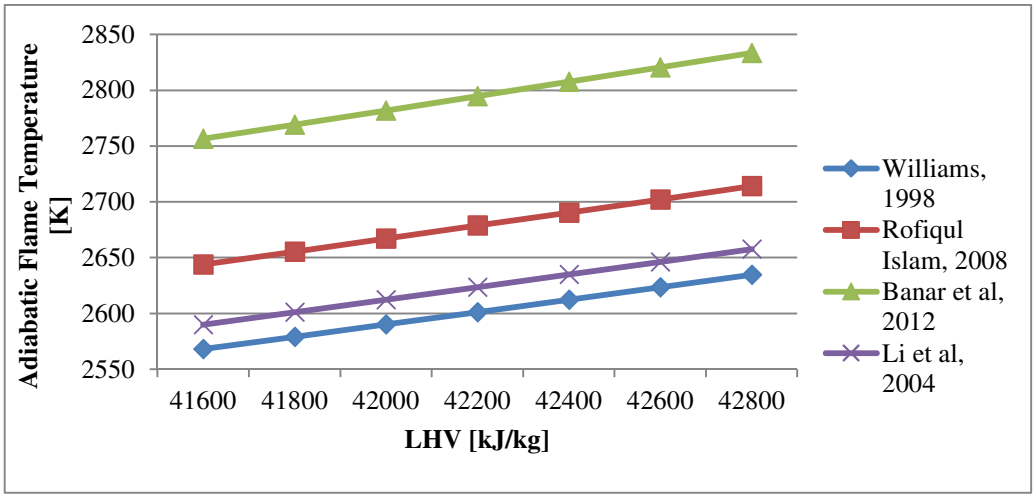

Figure 2. Correlation between T_{ad} and LHV using specific heat.

6.2 Adiabatic flame temperature using enthalpy tables

Besides the method using specific heats, it is also possible to calculate the value of T_{ad} with the enthalpy tables, using the method of energy conservation. Considering Eq. (22):

$$h°_{fR} + \Delta h_R = h°_{fP} + \Delta h_P \tag{22}$$

Where:
$h°_f$ = enthalpy of formation (kJ/kmol)
Δh = sensible enthalpy (kJ/kmol)

Since the enthalpy of formation of N_2 and O_2 is considered zero, resulting in $h°_{fR} = h°_{TPO}$. Also, knowing that the temperature of the reactants is 298K, we can conclude that $\Delta h_R = 0$. Therefore, eq. (23) shows the resulting equation:

$$h°_{f,TPO} = h°_P + \Delta h_P \tag{23}$$

Therefore, using the enthalpy of formation for the TPO found on the previous section, $h_{f,TPO}$=158264.1 kJ/kmol, with α=1, the adiabatic flame temperature is in between 2500K and 2600K, with interpolation this value is 2555.5K. Figure (3) shows the correlation between T_{ad} and LHV for TPO for various amounts of air excess, for composition reference [Williams et al, 1998].

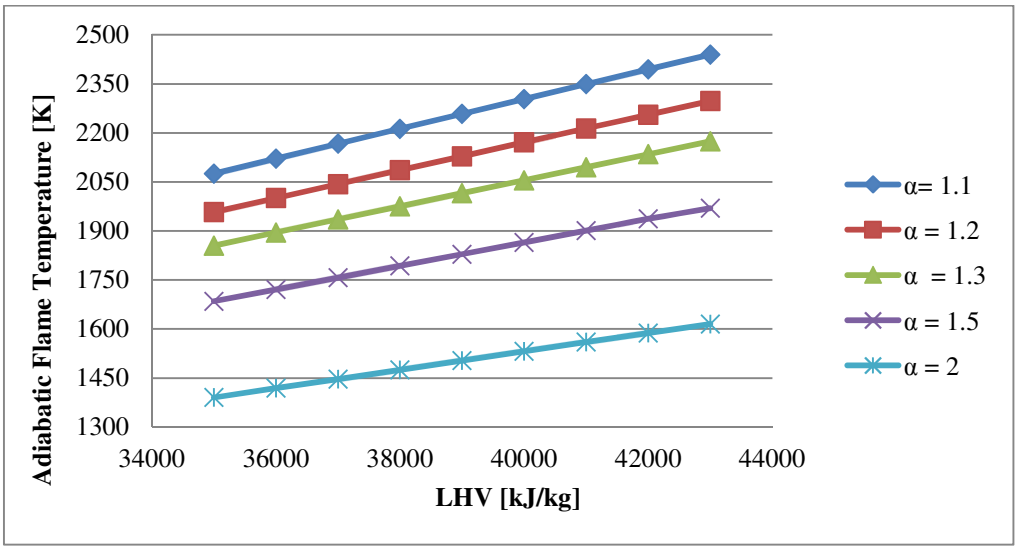

Figure 3. Correlation between T_{ad} and LHV for different values of air excess

7. CONCLUSIONS

The oil obtained by pyrolysis of waste tires because of their high calorific value (slightly less than that of fossil fuels), represents an opportunity to use in internal combustion engines. Some studies have already been made in this regard, advising blending with conventional diesel and / or biodiesel. Therefore, it is an interesting alternative to verify this oil by burning it in other thermal equipments (boilers, furnaces, combustion chambers, etc.) that the Brazilian industry can use, because its liquid state shows great advantages of storage, transport and atomization.

TPO emits 2.94 [ton of CO_2/m^3fuel], while diesel emits 2.64 [ton of CO_2/m^3fuel]. This difference is due to the greater presence of carbon in TPO than diesel. It is possible that this amount would be reduced if TPO is also mixed with biodiesel, which has reduced carbon emissions than diesel due to the closed carbon cycle of this renewable fuel.

The calorific value for both TPO and diesel is very similar, which is around 42 MJ/kg, this is found in various references and it means that the mixture of TPO with diesel will not decrease fuel power.

Another big difference between TPO and diesel is the amount of sulfur contained in TPO, which is substantial. While diesel only has about 1100-7000 ppm [Rofiqul Islam, 2008], the amount of sulfur contained in TPO varies from 0.1-1.55% in weight of fuel mass, although the difference in sulfur content is reduced when using methods of desulfurization and a smaller fraction of TPO mixed with diesel. Whereas renewable fuels do not have sulfur in their chemical composition, the mixture of TPO with Biodiesel, for example, would lead to a reduction of SO_2 emissions.

On the other hand, T_{ad} is shown to be very similar for TPO and diesel; calculated at 2381.1 K for diesel and about 2590 K for TPO at stoichiometric conditions.

TPO has shown to have very similar proprieties to diesel, such as calorific value, density and adiabatic flame temperature, therefore the second part of this study will be an experimental analysis of the atomization of TPO mixed with diesel with different types of atomizers.

8. ACKNOWLEDGEMENT

The authors wish to thank CNPq – Brazil (Proc. N°442050/2014-3) and FAPEMIG – Brazil (Proc. N° TEC APQ 01947-14) for their collaboration and support in the development of this work.

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