EMULSIFICATION OF WASTE COOKING OILS AND FATTY ACID DISTILLATES AS DIESEL ENGINE FUEL

Eliezer Ahmed Melo-Espinosa^{1*}, Ramón Piloto-Rodríguez¹, Leonardo Goyos-Pérez¹ and Sebastian Verhelst²

¹ Center for the Study of Renewable Energy Technologies, Faculty of Mechanical Engineering, Instituto Superior Politécnico "José Antonio Echeverría" (CUJAE), Cuba

² Department of Flow, Heat and Combustion Mechanics, Faculty of Engineering and Architecture, Ghent University, Belgium

* Corresponding author: emelo@ceter.cujae.edu.cu, eliezer.ahmed.melo.espinosa@gmail.com, Instituto Superior Politécnico "José Antonio Echeverría" (CUJAE), Calle 114 s/n, 19390, Cuba

KEYWORDS

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ABSTRACT

The scope of this paper is to analyze the possibilities and feasibilities, as well as the main experimental results reported about the emulsification method applied to waste cooking oils and fatty acid distillates as diesel engine fuels, compared with other commonly used methods. These waste products are obtained in the refining oil industry, food industry and service sector from the frying process, mainly. However, they are a little used as feedstocks to produce biofuels and constitute a potential source of contamination. From the review of the state of arts, significant decreases in exhaust emissions of nitrogen oxides, cylinder pressure, as well as increases of the ignition delay, brake specific fuel consumption, hydrocarbon, smoke opacity, carbon monoxide, particulate matters to emulsified waste cooking oils and fatty acid distillates compared with diesel fuel are reported. In some experiments the emulsified waste cooking oils achieved better performance than neat fatty acid distillates, neat waste cooking oils and their derivates methyl esters.

INTRODUCTION

Since fossil fuels increase greenhouse gas emissions and cause global warming, the use of alternative resources like biofuels are more pronounced everyday (Ozbay et al., 2008). For this reason, recently much attention has been paid to the development of alternative fuels in order to meet the emission standards and to reduce the dependency on fossil fuel (Kannan and Anand, 2011; Melo et al., 2014), as well as to counteract the recent changes in fossil fuels' prices and their influence on the energy worldwide scenario. In this context, taking into account the biodiversity and the "food vs. fuel" debate in mind (Singh and Singh, 2011), special attention has been paid to feedstocks such as non-edible vegetable oils and waste products (e.g. fatty acid distillates and waste cooking oils).

Although previous researches (Al-Widyan et al., 2002; Dorado et al., 2003; Cetinkaya and Karaosmanoglu, 2005; Pugazhvadivu and Jeyachandran, 2005; Felizardo et al., 2006; Sudhir et al., 2007; Chhetri et al., 2008; Lapuetra et al., 2008; Ozsezen et al., 2008; Giraçol et al., 2011; Kalam et al., 2011; Kartina and Suhaila, 2011; Murlidharan and Vasudevan, 2011; Galle et al., 2012; Elshaib et al., 2014; Ferrer and Piloto, 2014; Hirkude et al., 2014; Melo et al., 2014; Piloto et al., 2014; Piloto et al., 2014) using waste cooking oils (WCOs) and fatty acid distillates (FADs) have demonstrated that their use as feedstocks to produce biofuels is possible, their use is not common yet and represent a potential source of contamination. However, with their uses it is possible to reduce their effects on environment due to the dumping on rivers and seas. In addition, their exploitations to produce biofuels and energy might improve the efficiency in the refining oil, food and service industries (restaurants, hotels and food factories), adding values to these byproducts and contributing to the concept of reaching zero-waste.

On the other hand, WCOs and FADs are potential alternatives for diesel engines due to their very similar properties to diesel fuel. However, the direct use of WCOs and FADs might bring several problems in engine performance and emissions. These problems are mainly associated to a lower heating value and cetane number of WCOs compared to diesel fuel. Also, properties as kinematic viscosity and surface tension have a significant influence on the injection process as well as the process of mixture formation in diesel engines (Kruczynski ,2013; Melo et al., 2014).

From the above reasons exposed and to obtain a more engine-friendly fuel, is necessary to change the biofuels properties applying different methods such as: preheating, blending, dual fuel operation, transesterification, cracking/pyrolysis or emulsification (Melo et al., 2014). Among these methods, the emulsification techniques applied to WCOs and FADs

have not been studied thoroughly. The scope of this paper is to analyze the possibilities and feasibilities, though the main experimental results reported about emulsification method applied to WCOs and FADs compared with other commonly used methods.

WASTE PRODUCTS AS BIOFUEL'S FEEDSTOCKS

One of the most important challenges for the industrial sector dedicated to refining oil, service and food industry is to find solutions to use, reduce or eliminate large quantities of waste products generated from themselves. The waste cooking oils and fatty acid distillates are available around the world and generally have a low commercial value and a little use. The FADs from the refining oil industry are obtained, as is in Fig.1 showed.

Despite the WCOs are used for soap and animal feed productions, in agreement with Chhetri (Chhetri et al., 2008) part of they are discharged into the environment. Also, it is important to take into account that the use of WCO in the production of animal feeds in few countries is prohibited and this has resulted in the availability of surplus quantity WCO (Pugazhvadivu and Jeyachandran, 2005). In addition, the reuse of cooking oils might cause serious difficulties on human health. Due to the high temperatures, carcinogens as benzopyrene are released.





According to the composition, WCOs and FADs are suitable for the production of biofuels (see Table 1) increasing the efficiency to the above industries mentioned; contributing to the concept of reaching zero-waste concerning the utilization of by-products generated in the oil refineries (Piloto et al., 2013), reducing the environmental degradation (Pugazhvadivu and Jeyachandran, 2005). In agreement, researchers as Kartina and Suhaila (Kartina and Suhaila, 2011) refer that WCO is the cheapest source and can reduce problems on waste oil disposal whereas FAD is a byproduct from oil refining, therefore can be a readily available feedstock to produce engine biofuels.

However, the direct use of these waste products as engine fuel might affect the engine assessment and components. In order to obtain an economic and environmentally-friendly engine fuel from renewable feedstocks such as vegetable oils and animal fats, it is necessary to change the biofuels' properties (e.g.: viscosity, surface tension, free fatty acid, etc.). For this reason, different methods have been used, such as preheating, blending, dual fuel operation, transesterification, cracking/pyrolysis and emulsification. Among these methods, Demirbas et al. (Demirbas and Fatih, 2010) and Meher (Meher et al., 2006) specified that the transesterification is the most promising solution to the high viscosity problem and is an interesting method to produce a cleaner and environmentally safe fuel.

Transesterification of triglycerides produces biodiesel and proceeds through a reaction with alcohols in the presence of a catalyst and producing glycerol as a co-product (Attaphong, 2012). Biodiesel also has drawbacks, including cold weather limitations due to a relatively higher cloud point and pour point, and might increase emissions of nitrogen oxides (NOx) (Attaphong, 2012). Atmanli (Atmanli et al., 2013) and Agarwal (Agarwal and Rajamanoharan, 2009) pointed out that the transesterification process is a relatively expensive chemical process since it involves the use of chemicals, catalysts and a heating process. Also, depending on the quality of the feedstock (free fatty acids, glyceride and moisture content), different steps are necessaries.

The free fatty acids (FFA) is hydrolysis/oxidation by-products of oil due to cooking and storage, and monoglyceride and diglycerides are degrade products of oil (Chai et al., 2014). The free fatty acids and glyceride content in fatty acid distillates and waste cooking oils from different feedstocks are shown in Table 2. Due to the high free fatty acids (FFAs) content of WCO and FAD, these sources cannot be converted directly to biodiesel via alkaline transesterification (Kartina and Suhaila, 2011). Although different methods to decreases FFA and glyceride content are reported (Chongkhong et al., 2009; Kombe et al., 2013; Talebian-Kiakalaieh et al., 2013) in order to improve the transesterification efficiency, economically the biodiesel productions are not profitable.

Table 1:Physical-chemical properties of WCO and FAD (Yoshimoto et al., 1999; Kerihuel et al., 2005; Pugazhvadivu and Jeyachandran, 2005; Nanthagopal and Subbarao, 2009; Atmanli et al., 2013; García et al., 2013; Qi et al., 2013; Gandón et al. 2014: Senthil and Jaikumar. 2014)

Gandon et al., 2014, Sentin and Jarkunai, 2014)						
Properties	WCO	FAD (from Soybean)	Diesel Fuel			
Viscosity (<i>cSt</i>)	33,40-43,36	38,10	3.9-4.6			
Density (g/cm^3)	0,88-0,925	0,923	0.829-0.84			
Flash Point ($^{\circ}C$)	210-302	232	67.5-78			
Moisture Content (%)	0,2433-0.0693	0,3869	NS			
LHV (<i>MJ/Kg</i>)	36.47-39.60	NS	42.39-43.38			
Cetane number	33.4-37	NS	45-60.5			
C (w/w%)	76.8	NS	84-87			
H (w/w%)	11.6	NS	16-33			
O (w/w%)	10.6	NS	0			
Fatty acid composition (% wt)						
Myristic	NS	0,106-0,108				
Palmitic	NS	12,45-12,81				
Palmitoleic	NS	0,108-0,166				
Stearic	NS	3,79-3,89				
Oleic	NS	23,33-23,36				
Linoleic	NS	51,67-51,94				
Linolenic	NS	6,34-6,39				

NS: Not specified

Table 2: Free fatty acids and glyceride content in WCO and FAD from different feedstocks

Туре	Foodstocks	FFA	Glycerides	Ref.	
	recustocks	(wt %)	(wt %)		
FAD	Cotton	85.0	NS	(Keskin et al., 2008)	
	Palm	70.0-93.0	20-30	(Chongkhong et al., 2009; Budiman et al., 2012)	
	Hazelnut	45-50	NS	(Usta et al., 2005)	
	Soybean	30.1-45.4	13.0-23.3	(Hirota et al., 2003; Dumont and Narine, 2008;	
				Gunawan et al., 2008)	
	Rapeseed	48.8	32.9	(Liu and Wang 2009)	
WCO	NS	5-37.96	54.4-96.2	(Wang et al., 2006; Chhetri et al., 2008; Patil et	
				al., 2012; Wang et al., 2012; Kombe et al., 2013;	
				Chai et al., 2014)	

FFA: free fatty acids, FAD: fatty acid distillate, WCO: waste cooking oil, NS: Not specified

EMULSIFICATION METHOD APPLIED TO WASTE COOKING OILS AND FATTY ACID DISTILLATES

An alternative to the transesterification process may be the use of the emulsification method. Emulsification is the process of dispersing one liquid in a second immiscible liquid using a third substance known as emulsifier. Through this process, a dispersed system is obtained containing small droplets of water suspended in WCO or FAD. Emulsification is a simple process and might need no modification of the original engine design (Senthil et al., 2006).

Emulsions are interesting as fuel in diesel engines due to their simultaneous reduction of smoke and NOx emissions using vegetable oils/diesel as fuel (Yoshimoto et al., 1999; Lin and Wang, 2004; Senthil et al., 2006). Additionally, due to the microexplosion phenomenon, it is also possible to recover in some proportion the decrease in combustion efficiency.

Different researches about the formulation of emulsified biofuels using WCO or FAD reported the use of surfactants of the Span series and mainly co-surfactants such as ethanol. However, it is possible to use other surfactants with a hydrophilic-lipophilic balance (HLB) between 4-6 (Debnath et al., 2013), as well as short-chain alcohols as co-surfactants with the aim to increase the water amount and/or to futher improve the stability of the emulsified biofuels. The characteristics of some surfactants and co-surfactants used as emulsifier agents are shown in Table 3.

Chemical name	Chemical	HLB	FP	CN	Density	Ref.
	formula		(° <i>C</i>)		(g/mL)	
Sorbitan monopalmitate (Span 40)	$C_{22}H_{42}O_6$	6.7	NS	NS	NS	(Chow and Ho. 1996; Muñoz et al., 2007)
Sorbitan monostearate (Span 60)	$C_{24}H_{46}O_{6}$	4.7	NS	NS	NS	(Muñoz et al., 2007)
Sorbitan monooleate (Span 80)	C ₂₄ H ₄₄ O ₆	4.3	NS	NS	0.99	(Kerihuel et al., 2005; Kannan and Gounder, 2011; Attaphong and Sabatini, 2013)
Sorbitan sesquiolate (Span 83)	$C_{66}H_{130}O_{18}$	3.7	NS	NS	0.95	(Kerihuel et al., 2005; Mura et al., 2012; Attaphong and Sabatini, 2013)
Ethanol	C ₂ H ₅ OH	NS	10.2-13.5	5-8	0.788	(Qi et al., 2010; Tangka, 2011)
Bioethanol	C ₂ H ₅ OH	NS	13	NS	0.79	(Barroso et al., 2010)

Table 3: Surfactants and co-surfactants used in emulsified biofuels' formulation

FP: Flash Point,, CN: Cetane number, NS: Not specified

Researchers such as Morais et al. (Morais et al., 2006), Porras (Porras et al., 2008) and Bhimani (Bhimani et al., 2013) point out that a mixture of hydrophilic and hydrophobic surfactants yields a more stable emulsion. For this reason, in order to obtain a mixture of surfactants with HLB number according to the interval previously recommended, a mathematical equation given by Mollet (Mollet and Grubenmann, 2001) and Bhimani (Bhimani et al., 2013) can be used. Through this equation, the mass percentage (%) of the surfactants involved in the mixture can be obtained.

%Surfactant A = $[100 \cdot (X-HLB_B)] \cdot (HLB_A - HLB_B)^{-1}$ (1)

%Surfactant B=100 - %Surfactant A (2)

With:

X: HLB required

HLB_A: hydrophilic-lipophilic balance of the surfactant A HLB_B: hydrophilic-lipophilic balance of the surfactant B

An accurate methodology in order to formulate emulsified biofuels is difficult to establish because there are different feedstocks and different methods of preparation such as mechanical stirrer or membrane emulsification. Among these methods, the use of dispersion has been the most applied. Different researchers (Waltra, 1993; Khumar, 1996; Kerihuel et al., 2006) noticed that the higher rotational speed leads to the formation of smaller water droplets.

As was previously mentioned, the emulsification techniques applied to WCOs and FADs have not been studied thoroughly. However, researchers as Yoshimoto, Mubarak, Nanthagopal, Subbarao, Senthil and Jaikumar (Yoshimoto et al., 1999; Nanthagopal and Subbarao, 2009; Mubarak and Senthil, 2012; Senthil and Jaikumar, 2014) formulated emulsified biofuels using waste cooking oil (WCO). Yoshimoto (Yoshimoto et al., 1999) conducted an investigation about the emulsified WCOs, wish were discarded from restaurants and households. The emulsified WCO were prepared with different percentage of water (10-40%), 1% of surfactant (CRS-75) and a mixture in equal proportions of WCO and diesel fuel as continuous phase. The kinematic viscosity of emulsified WCO formulated increased exponentially with increasing of water content. According to stabilities test, emulsified WCO showed good stability, also it was better than emulsified WCOME.

Mubarak and Senthil (Mubarak and Senthil ,2012) prepared emulsified biofuels using WCO, ethanol, water and Span 80 as surfactant. The emulsions were prepared varying the amount of neat waste cooking oil, water and the ratio of surfactant/co-surfactant (Span 80/ethanol) in the system. These emulsified biofuels were prepared stirring vigorously. From the stability test, it was found that the mixture of 70% of WCO, 15% of water, 10% of ethanol and 5% of Span 80 was stable for two weeks (Mubarak and Senthil, 2012). The physical-chemical properties of emulsified biofuels formulated in both researches were not reported.

Senthil and Jaikumar (Senthil and Jaikumar, 2014) obtained their emulsions with specified amount of neat WCO, water, ethanol and Span 80 surfactant. From the stability test, it was found that the mixture of 70% of WCO, 15% of water, 10% of ethanol and 5% of surfactant by volume was stable for two weeks (Senthil and Jaikumar, 2014). On the other hand, Nanthagopal and Subbarao (Nanthagopal and Subbarao, 2009), using high-speed stirrer prepared their emulsions with diesel fuel-WCO mixture (equal quantities), different water amount (10, 20 and 30%) and surfactant. The physical-chemical properties of the emulsions in both studies were not reported.

On the other hand, emulsified FADs from soybean were formulated by Melo (Melo et al., 2014). The emulsified FADs were prepared as ternary systems using residual FAD, methanol anhydrous and the moisture content into FAD (see Table 1), take into account the less as possible stabilization time during the experiments. For this reason, a factorial design 23 was developed (selected factors analyzed: temperature, methanol percentage and intensity of agitation). The microemulsions formation was detected as the formation of one phase of a very clear, transparent and totally stable liquid system. The dynamic viscosity of emulsified FAD is 6.1 mPa \cdot s higher than the value found for the reference diesel fuel. The difference between neat FAD and emulsified FAD was 20.0 mPa \cdot s. The density measurements did not evidence significant differences among fuels.

PERFORMANCE AND EXHAUST EMISSIONS ASSESSMENT OF DIESEL ENGINES FUELLED WITH BIOFUELS FROM WCO AND FAD

The effects of the emulsified fuels on the engine performance are different from one study to another (Armas et al., 2005). The results obtained depend, mainly, on the engine operation mode (Castro et al., 1997; Samec et al., 2002), type and tuning of the injection system, and finally, on the optimized combustion chamber configuration (Armas et al., 2005). The physical-chemical properties of the emulsified fuel also play a significant role. A summary of the some experimental results reported about the use of WCO, FAD and their derivates compared with diesel fuel are show in table 4 and 5.

The WCO and FAD have a lower heating value, cetane number and poor volatility than diesel fuel (see Table 1) and their properties play an important influence on the premixed combustion phase. For this reason, differences in engine performance and exhaust emissions are expected, e.g. higher ignition delays for emulsified biofuels compared with diesel fuel and neat WCO, as was reported by Senthil, Jaikumar and Mubarak (Mubarak and Senthil, 2012; Senthil and Jaikumar, 2014). Generally, also the water content into emulsified biofuels delays the ignition.

Moreover, as a consequence of the lower heating value of the emulsified WCO and FAD, an increase of the specific fuel consumption was reported. In some experiments, the emulsified WCO achieved lower HC, CO and smoke opacity than neat WCO (Mubarak and Senthil, 2012) and diesel fuel (Nanthagopal and Subbarao, 2009). This behavior might be attributed to improvements on spray formation and the oxygen content into biofuels, despite adverse phenomena such as low temperature bulk quenching of the oxidation reactions, etc.

From the nitrogen oxide emissions reported (see Table 4 and Table 5), the use of emulsification method decreases the NOx emissions compared with diesel fuel, neat WCO, neat FAD and their derivates. This topic is one of the most important advantages to use the emulsification. An explication to these results is the thermal effect of the water on the combustion temperature. Nevertheless, formation of NOx is quite complex because numerous intermediate species exist (Imtenan, Varman et al. 2014). Similar results have been reported by different researchers (Crookes et al., 1995; Singh et al., 2010; Qi et al., 2013; Qi et al., 2013) using other feedstocks.

Finally, increases of the exhaust gas temperatures (Pugazhvadivu and Jeyachandran, 2005; Narayana et al., 2008; Hirkude et al., 2014) to WCOs and their derivates, compared with diesel fuel might be associated to slow combustion, the amount increases of fuel burned to meet the power requirement and the presence of the oxygen in the chemical

structure of these biofuels. Also, an important role plays in the case of WCOME the higher latent heat of vaporization of methanol, in concordance with Senthil et al. (Senthil, 2003).

Table 4: Performance and exhausts emissions assessment of diesel engines fuelled different biofuels from fad compared
with diesel fuel

		Performance, emissions and engine	Ref.
Туре	Engine	components wear	
Neat FAD (preheated at $70^{\circ}C$)	Petter	Slight differences in ignition delay	(Ferrer and Piloto
freat 171D (preneated at 70 C)	1-cylinder	Cylinder neak pressure	2014: Melo Piloto
Different blends (10,15, 25,	DI	t BSFC	et al., 2014; Melo et
50%) of FAD in diesel fuel		↓ NOx	al., 2014)
		↑ CO and HC	
Emulsified FAD	Petter	↑ BSFC	(Melo et al., 2014)
	1-cylinder	↓ NOx	
	DI		
Neat FAD	6-cylinder	↑ Dark deposits on the piston crown, the rings,	(Galle et al., 2012;
(preheated at $110^{\circ}C$)	DI	the combustion chamber and the injector.	Piloto et al., 2014)
		Heavy erosion produced by particles in the fuel	
		facilitates the start of microcracks, producing	
		fatigue loads and the failure of fuel injectors	

DI: Direct injection, FAD: fatty acid distillates, BSFC: brake specific fuel consumption, HC: unburned hydrocarbons, PM: particulate matter, CO: carbon monoxide, NOx: nitrogen oxides

Туре	Engine	Performance and emissions	Ref.
Neat WCOME	Deutz	\downarrow Cylinder pressure, Heat release rate and	(Elshaib et al.,
and two blends (70 and 30%) of	2-cylinders	Ignition delay	2014)
WCOME in diesel fuel	DI	\downarrow CO, HC	
		↑ NOx	
Different blends (10, 20, 30 and	1-cylinder	↑ BSFC and Cylinder peak pressure	(El-Kassaby and
50%) of WCOME in diesel fuel	DI	\downarrow BTE, CO and HC	Nemit-allah, 2013)
		↑ NOx	
Emulsified WCOME and	1-cylinder	↑ Kinematic viscosity with the increase of	(Yoshimoto et al.,
emulsified WCO-Diesel fuel in	DI	water amount	1999)
equal proportion (both emulsion		↓ NOx and Smoke density without worsening	
with 10, 20, 30 and 40% of water)		BSFC with water to fuel volume ratios	
Neat WCOME	Kirloskar	\downarrow BTE with the increases of WCOME in the	(Hirkude et al.,
and blends (90, 70 and 50%) in	1-cylinder	blends	2014)
diesel fuel	DI	\uparrow BSFC with the increases of WCOME in the	
		blends	
		↑ Exhaust gas temperature and Smoke opacity	
		with the increases of WCOME in the blends	
Neat WCO	Kirloskar	↑ BSEC, Exhaust gas temperature, CO and	(Pugazhvadivu
(preheated at 30°C, 75°C and	1-cylinder	smoke density	and Jeyachandran,
135°C)	DI	\downarrow BTE and NOx	2005)
Neat WCOME and blends of (10,	Kirloskar	↑ BSEC	(Subramaniam et
30, 50 and 70%) in diesel fuel	1-cylinder	\downarrow BTE and NOx	al., 2013)
	DI	↑ Smoke density	

Table 5: Performance and exhausts emissions assessment of diesel engines fuelled different biofuels from wco compared
with diesel fuel

Neat WCOME	Petter	↑ BSFC	(Gandón et al.,
	1-cylinder	↓ NOx and CO	2014)
	DI		
Different blends (25, 50 and 75%	TTF 8000s	↓ Smoke and HC	(Arslan, 2011)
) of WCOME in diesel fuel	4-cylinder	↑ CO and NOx	
	DI		
Neat WCOME and blends of (20,	Kirloskar	\downarrow Rate of heat release and BTE	(Narayana et al.,
40, 50 and 80%) in diesel fuel	1-cylinder	↑ Cylinder peak pressure and BSFC	2008)
	DI	\downarrow Ignition delay, CO and HC	
		↑ NOx and exhaust gas temperature	
Neat WCO (preheated at $70^{\circ}C$)	Petter	↓ Cylinder peak pressure	(Ferrer 2013;
and a blend of 15% of WCO in	1-cylinder	↑ Ignition delay at two experimental points	Gandón et al.,
diesel fuel	DI	(3.14 <i>KW</i> and 4.63 <i>KW</i>)	2014; Melo et al.,
		\uparrow BSFC, CO and HC	2014)
		↓ NOx	
Neat WCO and	Kirloskar	\downarrow Cylinder pressure. However, in three	(Mubarak and
Emulsified WCO	1-cylinder	experimental points the emulsified WCO was	Senthil, 2012;
(70% WCO, 15% water, 10%	DI	higher than neat WCO	Senthil and
ethanol and 5% Span 80)		↑ BSEC and Ignition delay	Jaikumar, 2014)
		\downarrow BTE and NOx	
		\uparrow HC, CO and Smoke opacity. In some	
		experimental points the emulsified WCO was	
		lower than neat WCO	
A blend of WCO in diesel fuel	DI	\downarrow BSFC, except to emulsified WCO-diesel	(Nanthagopal and
(equal quantities)		fuel with 30% of water	Subbarao, 2009)
		↑ BTE	
WCO-diesel fuel emulsions with		↓CO and NOx	
different water contents (10, 20		\uparrow PM and Smoke intensity	
and 30%)			

DI: Direct injection, WCOME: waste cooking oil methyl ester, BTE: break thermal efficiency, BSFC: brake specific fuel consumption, BSEC: brake specific energy consumption, HC: unburned hydrocarbons, PM: particulate matter, CO: carbon monoxide, NOx: nitrogen oxides

CONCLUSIONS

The review of state of the art developed here is an approach to emulsified waste cooking oils and fatty acid distillates with the aim of assemble experimental results reported in the scientific literature and enhancing the knowledge about this topic (formulation, characterization, engine performance and emissions). The investigations developed about the use of WCO and FAD as diesel engine fuel shown the transesterification as the method more commonly applied; in spite of the necessary step to remove the higher free fatty acid, glyceride and moisture content into FAD and WCO, as well as economic and environmental facilities that brings the emulsification method over other.

Studies focused on the analysis of formulation, stability and optimization of the FAD and WCO emulsification have been a little developed. In addition, the physical-chemical properties of emulsified biofuels formulated were not reported.

According to the engine performance and exhaust emissions, it is possible through the emulsification to use the FAD and WCO as engine biofuels. Differences between physical-chemical properties of FAD, WCO and diesel fuel are responsible of variations of the specific fuel consumption, ignition delay and exhaust emissions reported. Even the contribution of oxygen in the chemical structure of the biofuels, the water amount and the microexplosion process played their role. However, although the engine performance and exhaust emissions behavior depend on the physical-chemical properties of the emulsified biofuels, engine type and operation conditions but the exact relationship need to be further clarified.

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REFERENCES

Agarwal, A. K. and K. Rajamanoharan. 2009. "Experimental investigations of performance and emissions of Karanja oil and its blends in a single cylinder agricultural diesel engine." Applied Energy, Vol.86, 106-112.

Al-Widyan, M., G. Tashtoush, et al. 2002. "Utilization of ethyl ester of waste vegetable oil as fuel in diesel engines." Fuel Processing Technology, Vol.76, 91-103.

Armas, O., R. Ballesteros, et al. 2005. "Characterization of light duty Diesel engine pollutant emissions using wateremulsified fuel." Fuel, Vol.84, 1011-1018.

Arslan, R. 2011. "Emission characteristics of a diesel engine using waste cooking oil as biodiesel fuel." African Journal of Biotechnology, Vol.10, 3790-3794.

Atmanli, A., B. Yüksel, et al. 2013. "Experimental investigation of the effect of diesel-cotton oil-n-butanol ternary blends on phase stability, engine performance and exhaust emission parameters in a diesel engine." Fuel 109 503-511.

Attaphong, C. (2012). "Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel." Fuel, Vol. 94, 606-613.

Attaphong, C. and D. Sabatini (2013). "Phase behaviors of vegetable oil-based microemulsion fuels: The effects of temperatures, surfactants, oils, and water in ethanol." Energy Fuels, Vol. 27, 6773–6780.

Barroso, J., J. Ballester, et al. 2010. "Some considerations about bioethanol combustion in oil-fired boilers." Fuel Processing Technology, Vol. 91, 1537–1550.

Bhimani, S., J. Alvarado, et al. 2013. "Emission characteristics of methanol-in-canola oil emulsions in a combustion chamber." Fuel, Vol.113: 97-106.

Budiman, A., A. Lelyana, et al. 2012. "Biodiesel production from palm fatty acid distillate (PFAD) using reactive distillation." Journal Teknik Kimia Indonesia, Vol.11, 101-107

Castro, D., J. Alfonso, et al. 1997. Water/gas oil emulsions using residual as emulsifier. Emulsions World Conference, France, Proceedings of Emulsions World Conference.

Cetinkaya, M. and F. Karaosmanoglu. 2005. " A new application area for used cooking oil originated biodiesel: generators." Energy Fuels, Vol.19, 645-652.

Chai, M., Q. Tu, et al., 2014. "Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry." Fuel Processing Technology, Vol.125, 106-113.

Chhetri, A., C. Watts, et al. 2008. "Waste cooking oil as an alternate feedstock for biodiesel production." Energies, Vol. 1, 3-18.

Chongkhong, S., C. Tongurai, et al. 2009. "Continuous esterification for biodiesel production from palm fatty acid distillate using economical process." Renewable Energy, Vol.34, 1059-1063.

Chow, M. and C. Ho. 1996. "Properties of Palm-Oil-in-Water Emulsions: Effect of Mixed Emulsifiers." JAOCS, Vol.73, 47-53.

Crookes, R., F. Kiannejad, et al. 1995. "Seed-oil bio-fuel of low cetane number: the effect of water emulsification on diesel-engine operation and emissions." Journal of the Institute of Energy, Vol. 68, 142-151.

de Morais, J., O. Henrique, et al. 2006. "Physicochemical characterization of canola oil/water nanoemulsions obtained by determination of required HLB number and emulsion phase inversion methods." J Disper Sci Technol, Vol.27, 109-115.

Debnath, B., N. Sahoo, et al. 2013. "Adjusting the operating characteristics to improve the performance of an emulsified palm oil methyl ester run diesel engine." Energy Conversion and Management, Vol.69, 191-198.

Demirbas, A. and M. Fatih. 2010. Algae Energy: Algae as a New Source of Biodiesel, Ed. Springer.

Dorado, M., E. Ballesteros, et al. 2003. "Exhaust emissions from a diesel engine fueled with transesterified waste olive oil." Fuel, Vol. 82, 1311-1315.

Dumont, M. and S. Narine. 2008. "Characterization of soapstock and deodorizer distillates of vegetable oils using gas chromatography." Lipid Technology, Vol.20, 136-138.

El-Kassaby, M. and M. Nemit-allah. 2013. "Studying the effect of compression ratio on an engine fueled with waste oil produced biodiesel/diesel fuel." Alexandria Engineering Journal, Vol.52, 1-11.

Elshaib, A., M. Kamal, et al. 2014. "Performance of a diesel engine fueled by waste cooking oil biodiesel." Journal of the Energy Institute, Vol XXX, 1-7.

Felizardo, P., M. Correia, et al. 2006. "Production of biodiesel from waste frying oils." Waste Manage, Vol.26, 487-494.

Ferrer, N. 2013. Installation and Characterization of the Ceter's engine test bench. Workshop Biofuels produced in Cuba and their use in Internal Combustion Engines, La Habana.

Ferrer, N. and R. Piloto. 2014. Uso de oleínas residuales en motores de combustión interna. Experiencias del proyecto Celula de conocimientos en el uso de biocombustibles en MCI. Ed. IDICT. La Habana.

Galle, J., S. Verhelst, et al. 2012. "Failure of fuel injectors in a medium speed diesel engine operating on bio-oil." Biomass and Bioenergy.

Gandón, J., M. García, et al. 2014. Producción de biocombustibles a partir de aceite usado en la elaboración de alimentos. Experiencias del proyecto Célula de conocimientos en el uso de biocombustibles en MCI. Ed. IDICT. La Habana.

García, M., J. Gandón, et al. 2013. "Estudio de la obtención de biodiesel a partir de aceite comestible usado." Tecnología Química, Vol. XXXIII, 134-138.

Giraçol, J., Cristina, et al. 2011. "Reduction in ecological cost through biofuel production from cooking oils: an ecological solution for the city of Campinas, Brazil." Journal of Cleaner Production, Vol.19, 1324-1329.

Gunawan, S., N. Kasim, et al. 2008. "Separation and purification of squalene from soybean oil deodorizer distillate." Separation and Purification Technology, Vol.60, 128-135.

Hirkude, J., A. Padalkar, et al. 2014. "Investigations on the effects of Waste fried oil methyl ester blends and load on performance and smoke opacity of diesel engine using response surface methodology." Energy Procedia, Vol.54, 606-614.

Hirota, Y., T. Nagao, et al. 2003. "Purification of steryl esters from soybean oil deodorizer distillate." JAOCS, Vol. 80, 341-346.

Imtenan, S., M. Varman, et al. 2014. "Impact of low temperature combustion attaining strategies on diesel engine emissions for diesel and biodiesels: A review." Energy Conversion and Management, Vol.80, 329-356.

Kalam, M., H. Masjuki, et al. 2011. "Emission and Performance characteristics of an indirect ignition diesel engine fulled with waste cooking oil." Energy, Vol.36, 397-402.

Kannan, G. and R. Anand. 2011. "Experimental investigation on diesel engine with diestrol-water micro emulsions." Energy, Vol.36, 1680-1687.

Kannan, T. and M. Gounder. 2011. "Thevetia peruviana biodiesel emulsion used as a fuel in a single cylinder diesel engine reduces NOx and smoke." Thermal Science, Vol.15, 1185-1191.

Kartina, A. and M. Suhaila, 2011. Conversion of waste cooking oil (WCO) and palm fatty acid distillate (PFAD) to biodiesel. Sustainable Energy & Environment (ISESEE), 3rd International Symposium & Exhibition in Melaka IEEE 42 - 44

Kerihuel, A., K. Senthil, et al. 2005. "Investigations on a CI Engine Using Animal Fat and Its Emulsions With Water and Methanol as Fuel." SAE Technical paper, No. 2005-01-1729.

Kerihuel, A., M. Senthil, et al. 2005. "Use of animal fats as CI engine fuel by making stable emulsions with water and methanol." Fuel, Vol.84, 1713-1716.

Kerihuel, A., M. Senthil, et al. 2006. "Ethanol animal fat emulsions as a diesel engine fuel – Part 1: Formulations and influential parameters." Fuel, Vol.85, 2640-2645.

Keskin, A., M. Guru, et al. 2008. "Using of cotton oil soapstock biodiesel-diesel fuel blends as an alternative diesel fuel." Renewable Energy, Vol.33, 553-557.

Khumar, S. 1996. "On phase inversion characteristics of stirred dispersions." Chemical Engineering Science, Vol.51, 831-834.

Kombe, G., A. Temu, et al. 2013. "Pre-treatment of high free fatty acids oils by chemical re-esterification for biodiesel production-a review." Advances in Chemical Engineering and Science, Vol.3, 242-247.

Kruczynski, S. 2013. "Performance and emission of CI engine fuelled with camelina sativa oil." Energy Conversion and Management, Vol.65,1-6.

Lapuetra, M., J. Herreros, et al. 2008. "Effect of the alcohol type used in the production of Waste cooking oil biodiesel on diesel performance and emissions." Fuel, Vol.87, 3161-3169.

Lin, C.-Y. and K.-H. Wang. 2004. "Diesel Engine Performance and Emission Characteristics Using Three Phase Emulsions as Fuel." Fuel, Vol.83, 537-545.

Liu, Y. and L. Wang. 2009. "Biodiesel production from rapeseed deodorizer distillate in a packed column reactor." Chemical Engineering and Processing: Process Intensification, Vol.48, 1152-1156.

Meher, L., D. Vidya, et al., 2006. "Technical aspects of biodiesel production by transesterification—a review." Renewable and Sustainable Energy Reviews, Vol.10, 248-268.

Melo, E., R. Piloto, et al. 2014. "Performance of a single cylinder diesel engine fuelled with emulsified residual oleins and standard diesel fuel." Renewable Energies and Power Quality Journal, Vol. 12.

Melo, E., Y. Sánchez, et al. 2014. El escenario energético cubano y los combustibles alternativos. Experiencias, potencialidades y perspectivas futuras. Experiencias del proyecto Celula de conocimientos en el uso de biocombustibles en MCI. Ed. IDICT. La Habana.

Melo, E., Y. Sánchez, et al. 2014. "Surface tension prediction of vegetable oils using artificial neural networks and multiple linear regression." Energy Procedia, Vol.57, 886-895.

Mollet, H. and A. Grubenmann. 2001. Formulation technology – emulsions, suspensions, solid forms. Germany, Ed. Wiley-VCH.

Mubarak, M. and M. Senthil, 2012. An experimental study on waste cooking oil and its emulsions as diesel engine fuel Advances in Engineering, Science and Management (ICAESM), Nagapattinam, Tamil Nadu

Muñoz, J., M. Alfaro, et al. 2007. "Avances en la formulación de emulsiones." Grasas y Aceites, Vol.58, 64-73

Mura, E., C. Josset, et al. 2012. "Experimental study of the water in oil emulsions features by differential scanning calorimetry analysis." Applied Energy, Vol.97, 834-840.

Murlidharan, K. and D. Vasudevan. 2011. "Performance, emission and combustion characteristics of a variable compression ratio engine using methyl esters of waste cooking oil and diesel blends." Applied energy, Vol.88, 3959-3968.

Nanthagopal, K. and R. Subbarao, 2009. "Experimental investigation and performance evaluation of DI diesel engine fueled by waste oil-diesel mixture in emulsion with water." Thermal Science, Vol.13, 83-89.

Narayana, G., S. Sampath, et al. 2008. "Experimental studies on the combustion and emission characteristics of a diesel engine fuelled with used cooking oil methyl ester and its diesel blends." International Scholarly and Scientific Research & Innovation, Vol.2, 493-499.

Ozbay, N., N. Oktar, et al. 2008. "Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins." Fuel, Vol. 8, 1789-1798.

Ozsezen, N., M. Canakci, et al. 2008. "Performance and combustion characteristics of a DI diesel engine fueled with waste palm oil and canola oil methyl esters." Fuel, Vol.88, 629-636.

Patil, P., V. Gude, et al. 2012. "Biodiesel production from waste cooking oil using sulfuric acid and microwave irradiation processes." Journal of Environmental Protection, Vol.3, 107-113.

Piloto, R., E Melo et al. 2013. "Engine performance of a single cylinder direct injection diesel engine fuelled with blends of Jatropha Curcas oil and standard diesel fuel." Renewable Energies and Power Quality Journal, Vol. 11.

Piloto, R., E. Melo, et al. 2014. "Conversion of by-products from the vegetable oil industry into biodiesel and its use in internal combustion engines: a review." Brazilian Journal of Chemical Engineering, Vol.31, 287 - 301.

Piloto, R., E. Melo, et al. 2014. "By-products from the vegetable oil industry as a feasible source for biofuels production and pollution reduction." Renewable Energy and Power Quality Journal, Vol.12.

Porras, M., C. Solans, et al. 2008. "Properties of water-in-oil (W/O) nanoemulsion prepared by a low-energy emulsifiaction method." Colloids Surf A, Vol.324, 181-188.

Pugazhvadivu, M. and K. Jeyachandran. 2005. "Investigations on the performance and exhaust emissions of a diesel engine using preheated waste frying oil as fuel." Renewable Energy, Vol.30, 2189-2202.

Qi, D., C. Bae, et al. 2013. "Combustion and emission characteristics of a direct injection compression ignition engine using rapeseed oil based micro-emulsions." Fuel, Vol.107, 570-577.

Qi, D., C. Bae, et al. 2013. "Preparation, characterization, engine combustion and emission characteristics of rapeseed oil based hybrid fuels." Renewable Energy, Vol.60: 98-106.

Qi, D., H. Chen, et al. 2010. "Combustion and emission characteristics of ethanol-biodiesel-water micro-emulsions used in a direct injection compression ignition engine." Fuel, Vol.89, 958-964.

Samec, N., B. Kegl, et al. 2002. "Numerical and experimental study of water/oil emulsified fuel combustion in a diesel engine." Fuel, Vol.81, 2035-2044.

Senthil, M., et al., 2003. "An Experimental Comparison of Methods to Use Methanol and Jatropha Oil in a Compression Ignition Engine." Biomass Bioenergy, Vol.25, 309-318.

Senthil, M. and M. Jaikumar. 2014. "A comprehensive study on performance, emission and combustion behavior of a compression ignition engine fuelled with WCO (waste cooking oil) emulsion as fuel." Journal of the Energy Institute, Vol.XXX, 1-9.

Senthil, M., A. Kerihuel, et al. 2006. "A comparative study of different methods of using animal fat as a fuel in a compression ignition engine." Journal of Engineering for Gas Turbines and Power, Vol.128, 907-914.

Singh, P., J. Khurma, et al. 2010. "Coconut Oil Based Hybrid Fuels as Alternative Fuel for Diesel Engines " American Journal of Environmental Sciences, Vol.6, 71-77.

Singh, P. and A. Singh. 2011. "Production of liquid biofuels from renewable resources." Progress in Energy and Combustion Science, Vol.37, 52-68.

Subramaniam, D., A. Murugesan, et al. 2013. "A comparative estimation of C.I. engine fuelled with methyl esters of punnai, neem and waste cooking oil." International Journal of Energy and Environment, Vol.4, 859-870.

Sudhir, C., N. Sharma, et al. 2007. "Potential of waste cooking oils as biodiesel feedstock." Emirates J Eng Res, Vol.12, 69-75.

Talebian-Kiakalaieh, A., N. Amin, et al. 2013. Biodiesel production from high free fatty acid waste cooking oil by solid acid catalyst. Proceedings of the 6th International Conference on Process Systems Engineering (PSE ASIA). Kuala Lumpur, 572-576.

Tangka, J, et al. 2011. "Physico-chemical properties of bio-ethanol/gasoline blends and the qualitative effect of different blends on gasoline quality and engine performance." Journal of Petroleum Technology and Alternative Fuels, Vol.2, 35-44.

Usta, N., E. Ozturk, et al. 2005. "Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine." Energy Conversion & Management, Vol.46, 741-755.

Waltra, P. 1993. "Principles of emulsions formation." Chemical Engineering Science, Vol.48, 333-349.

Wang, Y., S. Ma, et al. 2012. "Solid superacid catalyzed glycerol esterification of free fatty acids in waste cooking oil for biodiesel production." European Journal of Lipid Science and Technology, Vol.114, 315-324.

Wang, Y., S. Ou, et al. 2006. "Comparison of two different processes to synthesize biodiesel by waste cooking oil." Journal of Molecular Catalysis A: Chemical, Vol.252, 107-112.

Yoshimoto, Y., M. Onodera, et al. 1999. "Reduction of NOx, smoke and bsfc in a diesel engine fuelled by biodiesel emulsion with used frying oil." SAE Technical Paper, No. 1999-01-3598