American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-6, Issue-1, pp-56-67
www.ajer.org
Research Paper Open Access

Cetane Number Effect on Engine Performance and Gas Emission: A Review

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ABSTRACT: *Use of biodiesel fuel was considered as a panacea to high exhaust gas emission in compression ignition (CI) engines. The review reported high cetane number (CN) as an ignitionquality of biodiesel responsible for low carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) but increase in nitrogen oxide (NOx) emissions compared to conventional diesel. High CN wastraced to long straight carbon chain and low degree of unsaturation of the fatty acid of biodiesel feedstock. Also reported was that high CN of biodiesel was responsible forshorten ignition delay(ID)and increase in residence time of combustion process resulting incomplete combustion and resultant low emissions.Also CNincreases with molecular weight of the fatty acid and alcohols moiety, and when the position of carbonyl 'side-chain' is closest to the end of the molecular chain was reported. Methods of CN ratinglike use ofIgnition Quality Test (IQT) and use of two reference hydrocarbon compounds (long straight-chain hydrocarbon, hexadecane ($C_{16}H_{34}$) and highly branched compound, 2,2,4,4,6,8,8,-heptamethylnonane (HMN), also $C_{16}H_{34}$) on cetane scale,which American Standard of Testing Material(ASTM D6751) and the European Standard (EN 14214)had adopted for the measurement of CN was reported. The review also discussed the suitable limits or ranges of CNs within which complete combustion and low gas emission are favoured. It concluded with ways to improve CN value like the use of additivesnamely 2-ethyl hexyl nitrate, alkyl nitrate, peroxide compounds, and methyloleate and effective refining process.*

Keywords:*Cetane number, exhaust gas emission, biodiesel property, fatty acid structure, ignition delay, engine performance.*

I. INTRODUCTION

Biodiesel is defined as the mono alkylesters of long chain fatty acids derived from renewable feedstock, such as vegetable oil or animal fats, with high CN for use in CI engine (Enaburekhan and Bello,2013). It is also defined as the prime indicator of the quality of fuel used in internal combustion engines (Rao, 2011;Velmurugan and Gowthamn, 2012;Yanowitz et *al.*, 2014; Knothe, 2005). Again, it is viewed as a relative measure of the interval between the injection of the fuel into the cylinder and the onset of auto-ignition (Refaat, 2009).Marina *et al.*(2008) viewed CN as a complex function of the physicochemical characteristics of the fuel andagreed that its characteristics higher CNthan conventional diesel place it at comparative advantage in terms of fuel ignition quality in CI engines. Also Pankaj*et al.* (2016) posited that fuel combustion depends upon fuel CN, viscosity and density of the fuel. CN affects exhaust emissions indirectly by shorten or extended ID. Biodiesel shortens ID asa result of its high CN, which implies longer time for complete combustion to take place in the cylinder,with resultant low emissions.Extended ID is a result of low CN.Longer ID implies less time for complete combustion hence higher exhaust emission. This paper is a review of works done by different authors on CN, highlighting its importance as biodiesel fuel property to diesel engine performance as well as the exhaust gas emission implications.

II. EFFECTS OF CETANE NUMBER ON IGNITION DELAY AND EXHAUST EMISSION

Shahabuddin*et al.* (2013) posited that ID is governed by CN.The different stages of combustion are shown in Figure 1, while the extended view of ID is shown in Figure 2.Increase in CN shortens ID (that is, 'c'; Figure 2) such that there is early start of combustion (SOC, 'b'; Figure 2) thereby increasingthe residence time for complete combustion aided by rich oxygen content of biodiesel. The early SOC and shorter ID are attributed to higher CN. Both start of fuel injection (SOI) and SOC are important features as they affect the combustion characteristics, exhaust gas temperature and exhaust emissions of engines.Obed*et al.* (2014) contributed that an increase in CNcauses a shorter ID which results in less fuel being injected during the premix burn and more during the diffusion burn portion, thus reducing the cylinder pressure rise, which may result in lower cylinder temperatures. These characteristics lead to a complete combustion of biodiesel fuel with lower exhaust emissions compared to mineral diesel.

Knothe (2005),Refaat (2009), Alessandro (2009),Marina *et al.* (2007), Zhu *et al*, (2010),Jaffar*et al.* (2012),Yanowitz *et al.*(2014),Obed*et al.* (2014),Mohd*et al.* (2015),Miłosław (2016) and Pankaj*et al.* (2016) reported significant reductionof CO, PM, HC, exhaust emissions and higher nitrogen oxide (NOx) emissions with use of biodiesel compared to conventional diesel. Obed*et al.* (2014) pointed out few disadvantages of biodiesel fuel,as fuel injector joking, and oxidative degradation (auto oxidation) resulting from contact with atmospheric air during prolonged storage.

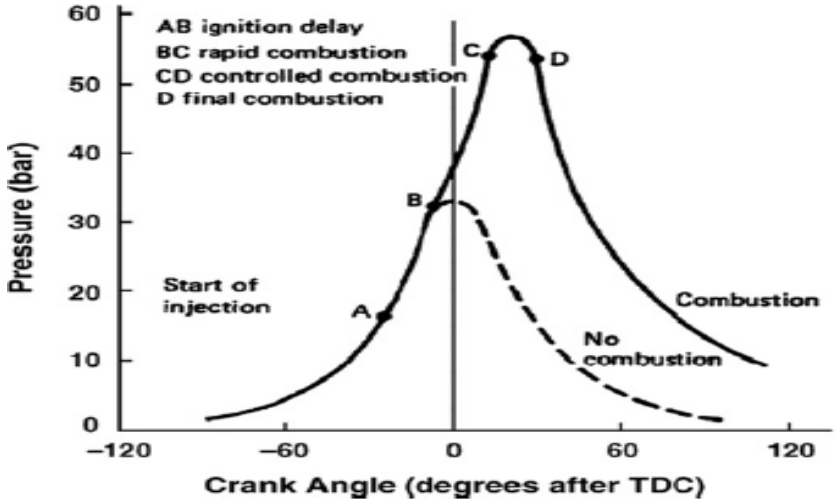

Figure 1: Different stages of combustion in CI engines.

Source: Shahabuddin*et al.*(2013)

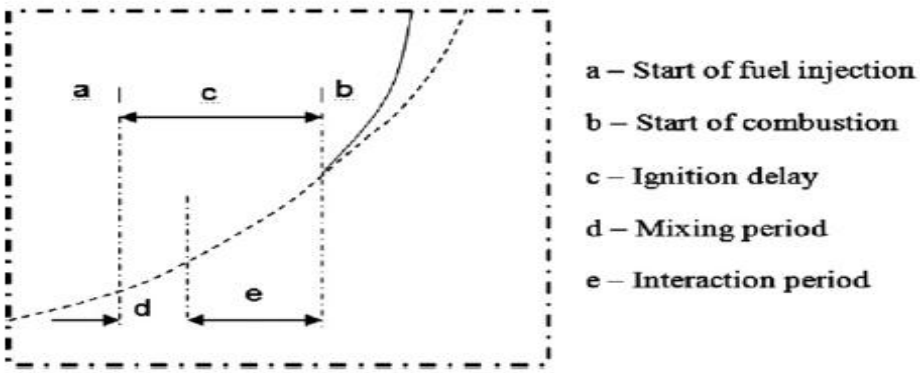

Figure 2: Extended view of ignition delay.

Source: Shahabuddin*et al.*(2013)

III. DETERMINATION OF CETANE NUMBER

Different methods for determining CN of fuel have been reported (Boerlage and Broeze, 1933; Knothe, 2005;Ramadhas*et al.*, 2006; Bangboye and Hansen, 2008; Barsamin, 2009; Alessandro, 2009; Refaat, 2009; Yanowitz et *al.*, 2014 andPankaj*et al.*, 2016).During the 1930s, Boerlage and Broeze (1933) of the Delft Laboratory in the Netherlands sought a procedure to determine the ignition quality of diesel fuel that was similar to the octane rating method for gasoline using two reference hydrocarbon fuels (Yanowitz et *al.*, 2014). The two

reference hydrocarbon compounds according to Knothe (2005) are along straight-chain hydrocarbon, hexadecane ($C_{16}H_{34}$) (with trivial name cetane) (see Figure 3)and a highly branched compound, 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also $C_{16}H_{34}$),(see Figure 4).On the cetane scale, the former is regarded asthe high quality standard with an assigned CN of 100, while the latteris of low-quality standard with poor ignition quality with an assigned CN of 15.Based on the two reference compounds, stipulated experimental procedures and standards asalready provided by ASTM D6751 and the European Standard EN 14214 were used for the measurement of their CN. The ASTM method for measuring CN is D613.The CNs of fuels can be computed with reference to n-hexadecane (cetane) and 2,2,4,4,6,8,8,-heptamethylnonane (HMN)fromequation (1) as:

$$\boldsymbol{CN = \%\ byvolumeofn - hexadecane + 0.15 * (\%\ byvolumeofHMN)} \quad \mathbf{1}$$

Figure3: Structure of n-hexadecane

Source: Yanowitz *et al.* (2014).

Figure4: Structure 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also $C_{16}H_{34}$),

Source: Yanowitz *et al.* (2014).

Yanowitz *et al.* (2014) highlighted that in some cases, CN data were not available for the pure compound, but were available for blends of a known volume of the pure compound in diesel fuel of known CN. In such cases, it is possible to compute a blending of CN. Assuming the CN of the blend is a linear combination of the CN of the components,it is expected that for a 10% blend its CN is expressed as equations (2) and (3):

$$\boldsymbol{BlendCN = (0.9) * (BasefuelCN) + (0.1) * (TestfuelCN)} \quad \mathbf{2}$$

Or; $$\boldsymbol{TestfuelCN = \frac{[(BlendCN) - (0.9) * (BasefuelCN)]}{0.1}} \quad \mathbf{3}$$

Hannu (2007) added that when a fuel has the same ID period as a mixture of the two primary reference fuels, its CN is derived from the volume percent of cetane and heptamethylnonane, expressed as equation (4):

$$\boldsymbol{CN = \%cetane + 0.15(\%heptamethylnonane} \quad \mathbf{4}$$

The use of IQT to determine CN has been reported (Barsamin 2009; Knothe 2005; Refaat 2009; Alessandro 2009;Yanowitz et *al.*,2014).Barsamin(2009) reported that IQTis a method that measures the time delay between the start of fuel injection and the start of significant combustionthrough auto-ignition of a pre-measured amount of diesel in a constant volume combustion chamber (CVCC).The time delay is used with aformula to calculate the derived cetane number (DCN) which correlates to the CN from that of the D613 cetane engine apparatus. Yanowitz *et al. (*2014) explained that because the CN determined by CVCC methods is not measured in the actual cooperative fuel research (CFR) engine, which is the defined source of CN values, the values that result from this approach are known as the derived cetane number (DCN).Knothe (2005) submittedthat CN of branched and straight-chain of fuel esters has been determined with the Ignition Quality Testerk (IQTk). Cetane numbers CNs obtained with the IQTkare referred to as CN_{IQT}. The IQTk, ID and CN are related by equation (5) (Knothe*t al.,* 2003) expressed as:

$$CN_{IQT} = 83.99\ X\ (ID - 1.512)^{-0.658} + 3.547 \quad \mathbf{5}$$

However, there are two ASTM test methods using IQT:D6890 and D7170 (Barsamin, 2009). The differences between them are the number of cycles run for the test (32 cycles for D6890 versus 25 cycles for D7170) and the averaging of results.Other methods for determination of CN are near infra-red (NIR) analyser (Barsamin, 2009), use of artificial neural network (ANN) Ramadhas*et al.*(2006);Bangboye and Hansen (2008),and the use of cetane indices (Barsamin, 2009.)

IV. FACTORSINFLUENCINGCETANE NUMBER

Knothe (2005) reported that some of the properties that influence CN included as specifications in standards can be traced to the structure of the fatty esters. Same was consented to by Zhu *et al.* (2010),Mohd*et al.* (2015), Marina *et al.* (2007),Jaffar*et al.* (2012) and Miłosław (2016). Therefore, as biodiesel consists of fatty acids esters, not only the structure of the fatty acids but also that of the ester moiety derived from the alcohol can influence the fuel properties. The properties of a biodiesel fuel that are determined by the structure of its component fatty esters include ignition quality, heat of combustion, cold flow, oxidative stability, viscosity and lubricity. The ignition quality is essentially determined by the CN (Rao, 2011).

i. Type of carbonyl chain

Two types of carbonyl chains (straight-chain or branched-chain) have been reported in fatty acid methyl ester FAME (Klopfenstein (1985); Harrington (1986);Agrawal and Das (2001); Marina *et al.* (2008)Refaat (2009), Jing (2011); Jinlin*et al.*(2011); Prem*et al.* (2014); Miłosław (2016). The fatty acids are almost entirely straight chain aliphatic monocarboxylic acids. The chain is built from two carbon units and *cis* double bonds inserted by desaturase enzymes at specific positions relative to the carboxyl group that give the even-chain-length fatty acids bonds. A large number of fatty acids, varying in chain length and unsaturation also result from this pathway.

The two reference compounds on the cetane scale show that CN decreases with decreasing chain length and increasing branching (Knothe, 2005). Generally, branching of the chain makes the molecule more compact and thereby decreases the surface area. Therefore, the intermolecular attractive forces which depend upon the surface area, also become small in magnitude. Consequently, the reactivity of the branched chain alkanes are less than the straight chain isomers. Again, other disadvantages of the branched esters are the higher price of the branched bonded alcohol and the changes needed in the transesterification process yielding the branched esters. Branched esters are of interest because they exhibit improved low-temperature properties (Knothe*et al*., 2003). Ladommatos*et al.* (1996a) had shown that a lower CN of fuel resulting from high branched chain can lead to higher peak cylinder gas temperatures, and thus a higher amount of thermal NOx formation during combustion.

Jing (2011) confirmed that the CN depends primarily on fuel structure (straight-chain or branched-chain), molecular weight, volatility, and the number of double bonds; that the higher CN biodiesel was due to longer carbon chain and a higher degree of unsaturation of the fuel. Shahabuddin*et al.* (2013) reported that CN, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. Refaat (*2009)* added thatbranched esters derived from alcohols such as iso-propanol have CN that are competitive with methyl or other straight-chain alkyl esters. Thus, one long straight chain suffices to impart a high CN even if the other moiety is branched. Marina *et al.,* (2008) noted that long chain saturated methyl esters have the highest CN while unsaturated methyl esters have the lowest. As the number of unsaturated carbon-carbon double bonds in a molecule increases, the adiabatic flame temperatures increase and therefore NOx emission increase. CN variation can also be the result of biodiesel degradation (as biodiesel ages, its CN can increase). Knothe*et al.,* (2003) investigated the effect of the molecular structure of pure fatty acid alcohol esters on the ignition quality of the molecules in a constant volume ignition quality tester (IQT). The experiments provided reliable absolute values of CN for 15 different fatty acid esters and four fatty acids. And was confirmed that the longer the chain length of the alcohol used in the transesterification process is, the higher the CN of the fuel molecule becomes, and that an increase in un-saturation of the fatty acid chain is correlated with a lower ignition quality. Again, for the four fatty acids; their ignition quality is lower than that of their respective monohydric alcohol esters.

Klopfenstein (1985) also confirmed that branching in the alcohol chain of the molecule significantly reduces the CN of the fuel. Inanengine experiments on real vegetable oils transesterified with different alcohols, he confirmed that transesterification with normal alcohols of increasing chain-length leads to progressively better ignition quality of the fuel. The experiments also provided confirmation that branching within the alcohol chain reduces ignition quality with respect to un-branched alcohol chains of the same atomic make-up under real diesel engine conditions. The results confirmed previously observed trends on chain lengths of the alcohol chain and the fatty acid chain (Jing, 2011;Shahabuddin*et al.*,2013).

Refaat (*2009*) reported that unsaturation in the fatty acid chain was again the most significant factor causing lower CN (Knothe*et al*., 2003).The more saturated the molecules, the higher the CN (Geller and Goodrum, 2004). A high value of CN was observed in saturated FAME such as palmitate and stearate, while the CN is in the medium range in mono-unsaturated FAME. Bangboye and Hansen (2008) verified that CN follows the same trend in the composition of the FAME compounds in all the feedstock used. It was observed that a feedstock that is high in saturated fatty esters has a high CN, while feedstock predominant in unsaturated fatty acid have lower CN values. This agrees with previous reports by Harrington (1986), van Gerpen (1996) and Knothe*et al*. (2003). This suggests a profound effect of fatty acid composition on the CN of the biodiesel.

ii. Molecular weight of carbonyl group

Klopfenstein (1985); Harrington (1986); van Gerpen(1996); Knothe*et al.* (1997); Marina *et al.* (2008); Refaat (*2009*); Jing (2011) reported the effect of mass of added molecular carbonyl bonds to CN. The experiment conducted according to ASTM D-613by Klopfenstein (1985) on the ignition quality of individual fatty acid alcohol esters in a single cylinder CFR engine observed that increasing the molecular mass of the fatty acid moiety of the molecule produced a larger increase in CN than increasing the molecular mass of the alcohol moiety of the molecule by the same amount. In addition, the raw fatty acids have lower CN than their monohydric alcohol esters because of increase molecular mass from alcohol moiety.

Alessandro (2009) investigated the influence of the fatty acid chain length, the alcohol chain length, and the number of double bonds of moleculeson CN.The effect of molecular mass of fatty acid alcohol esters on CN, demonstrating the influence of chain length of alcohol chain versus that of the fatty acid chain of the moleculewas shown in Figure 5. It revealed that as carbon number of ester increases, CN increases. The general outcome of the experiment indicated three important trends in the effect of the molecular structure of fatty acid esters on their ignition quality. They are:

- CN increases with molecular weight of the fatty acid moiety;
- CN increases with molecular weight of the alcohols moiety; and
- CN decreases with unsaturation of the fatty acid moiety.

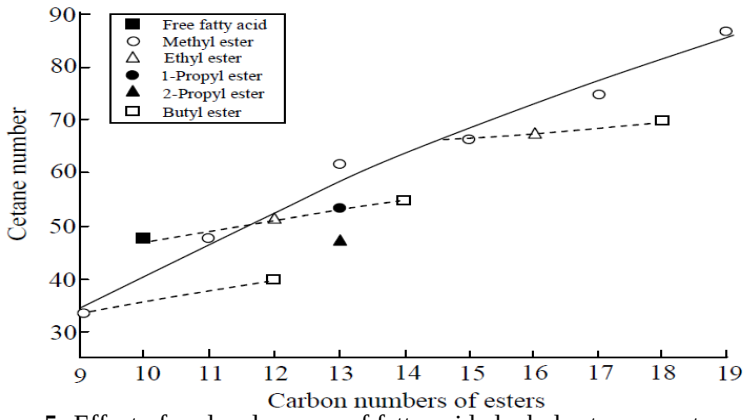

Figure 5: Effect of molecular mass of fatty acid alcohol esters on cetane number.
Source: Alessandro (2009).

The study McCormick *et al.* (2001) carried out on CN measurements of fuels showed that a decrease in fatty acid chain length and an increase in number of double bonds within the fatty acid moiety both resulted in a decrease of CN. This confirmed previous results obtained by (Klopfenstein 1983). It may thus be hypothesised that the results observed by Graboski*et al*. (2003) and McCormick *et al.* (2001) may be attributed to a large extent to differences in ignition quality of the various molecules (Alessandro, 2009).

iii. Position of attachment of the carbonyl group to molecular chain

Alessandro (2009) recorded that Harrington (1986) carried out qualitative predictions of the ignition quality of fatty acid alcohol esters with regards to their molecular structure. He pointed out that it is visible that the relative position of the carbonyl group on the fatty ester chain has a distinct effect on CN. Also, when he applied a correction in the CN due to the length of the fatty acid chain, derived from Klopfenstein's (1983) data, it was observed that a good correlation exists between the relative position of the carbonyl group within the chain and the CN. The cetane rating is highest when the carbonyl 'side-chain' is closest to the end of the molecular chain, and lowest as the side-chain approaches the mid-point of the chain or as the relative position (RP)is 0.5 of the chain length (see Figure 6).

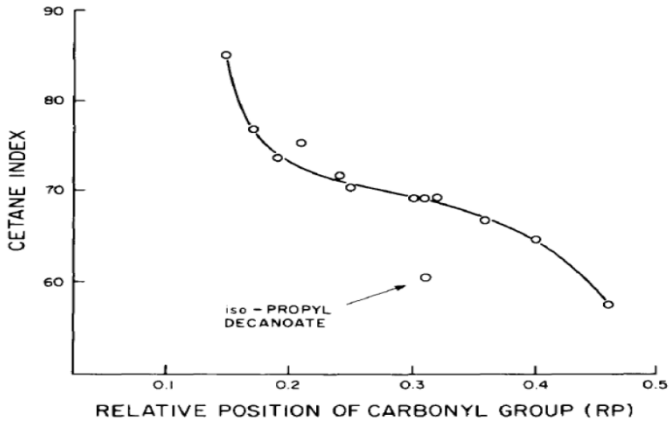

Figure 6: Effect of relative position of carbonyl group in a saturated fatty acid monohydric alcohol ester on cetane number.

Source: Alessandro (2009)

V. SUITABLE LIMITS OF CETANE NUMBER

There are ranges within which CN of fuels will satisfactorily favour early or retarded ignition in diesel engines (Rao, 2011; Jinlin*et al.*, 2011; Gordon and Mastorakos,*2011;* Hossain *et al*., 2015; Jing, 2011;Canakei and Van Gerpen2003; EPA 2002; and Wojciech*et al.*,2011).Outside the stipulated CN ranges there are bound to be emission implications. It would either favour high emission or lower emission.Sabah and Miqdam (2012) reported that too high or too low a CN can cause operational problem. If a CN is too high, combustion can occur before the fuel and air are properly mixed; resulting in incomplete combustion while too low CN can cause engine roughness, misfiring, higher air temperature, slower engine warm-up, and also incomplete combustion. Refaat (2009*)* confirmed that high CNs signify short ID between fuel injection and ignition.Sabah and Miqdam (2012); Knothe (2005);Pankaj*et al.*,(2016); Bangboye and Hansen(2008);and Yanowitz*et al.(*2014) confirmedRefaat(2009) assertion. Theyagree that low CNs tend to cause diesel knock and increased gaseous and particulate exhaust emissions because of incomplete combustion. Palash*et al.* (2013) and Hossain *et al.* (2012)confirmed thathigh CN results to shorten ID, which provides more time for the fuel combustion process to be completed, with resultant low exhaustemission.

An example of problem from low CN was observed by Wojciet*het al.* (2011). They recorded that in an experiment with rapeseed biodiesel, that too low values of the CN (below 45) worsen the engine operating conditions, caused extension of the self-ignition delay, excessive increase of pressure and temperature in the combustion chamber which consequently led to premature wearing up of the components and increase emission and smoke. Again, Knothe (2005) reported a wide variation in the values of the CN for biodiesel. He observed that the values of CN of soybean oil-derived biodiesel ranged from 45 to 60, while those of rapeseed oil-derived biofuel ranged from 48 to 61.2. Meanwhile, the admissible minimum value of the CN according to European requirements is 51 (EN14214) or47 (ASTM D6751) for biodiesel(Klopfenstein, 1985).CN of 51 was advocated for used in the moderate climates**.** Also, a minimum CN of 40 ASTM D975 has been accepted for conventional dieselfuel.Sabah and Miqdam (2012) also reported that in an experiment with conventional diesel, CN range from 40 to 55 operated satisfactorily, but there was no performance or emission advantage when the CN was raised past 55.The statement was confirmed by Velmurugan, and Gowthamn (2012).

Pankaj*et al.* (2016) contributed that biodiesel has superior physico-chemical properties than that of conventional diesel fuel, such as higher CN (> 58), flash point temperature (> 150 ºC), lubricity (350 µm), lower sulphur content (0.002 wt. %) and lower aromatics (almost zero).Experimental study conducted by Canakci and VanGerpen(2003) in John Deere 4276T model diesel engine using soybean oil methylester (SOME) and yellow grease methylester (YGME) showed that ID is governed by the CN, and cause variations in exhaust gas emission. The experimental results indicated the start of combustion (SOC) and shorten ID for SOME and YGME were 3.41 and 4.21 and 0.751 and 0.631 respectively than that of diesel fuel which was attributed to higher CN of 51.5 and 62.5 for SOME and YGME respectively as compared to conventional diesel of 42.6. The shorten ignition delay caused variations in exhaust emission level and soot. However, Shahabuddin*et al.* (2013)reported that the experiment conducted by Nwafor*et al.* (2000) recorded slightly lower CN for biodiesel whichexhibited longer delay periods as well as slower burning rate, hence resulting in delay of combustion, higher exhaust and lubricating oil temperatures.Higher speed diesels operate more effectively with higher CN fuels (Velmurugan and Gowthamn2012).

VI. EFFECTS OF CETANE NUMBER ON CO, HC, AND PMEMISSIONS

The review conducted by Jinlin*et al*.(2011)revealed that biodiesel has a higher CN, thus generally reduces CO emissions, HC and PM.The view is admitted by Karabektas(2009);Keskin*et al*.(2008); Kim and Choi (2010); Guru *et al*. (2010); Wu *et al*.(2009);Lertsathapornsuka*et al*.(2008); Pinto *et al*.,(2005); and Shi *et al*. (2005). The investigation by Ullman*et al*.(1990) on exhaust gas emission shows that among the fuel properties considered in their experiment,high values of CN wasa key to reducing HC and CO emissions. Also, the experiment conducted by Gabele*et al*. (1986) showed that high CN reduced COemission. In the test they compared the exhaust emissions of a "high quality" fuel (high CN and low aromatic content) with a "low quality" fuel (low CN and a high aromatic content) used in a diesel passenger car. Their results indicated a decrease of up to 40% in HC, and CO, with "high quality" fuel due to high CN number compared to low quality fuel with low CN and high aromatic content.

Prem*et al*. (2014) reiterated that the CN increase cause reduction in CO emission because majority of the experiments, reviewed indicated that for any increase in CN, there was reduction in ID, increased the injection pressure, thereby, making the fuel particles finer giving lower smoke and low CO emission. Same trend was reported by Wu *et al*. (2009), who investigated the difference in CO emissions among five biodiesels and diesel fuel. They concluded that CO decreased consistently for the five biodiesels, the blends and diesel fuel due to CN increased. In another engine performance test conducted by Bekal and Babu (2008) on sunflower biodiesel blends and Pongamia biodiesel blends emission. Sunflower biodiesel blend had higher CN and peak pressure than the Pongamia biodiesel blend, however indicated reduction in ID but with increased CO emission. The same trend was reported by Rehman*et al*. (2008) with karanja oil biodiesel.

Alessandro (2009)in his investigation subjected his fuel samples to three series of experiments: constant injection timing, constant ignition timing and constant IDto evaluatehow the fatty acid molecule chain length affects PM. He presented the result in a graph (shown in Figure 7). From the Figure, the longer chained molecules which imply high CN values produced higher number of very small particles which he interpreted to low PM. Also,as degree of unsaturation of the molecules which is reflected in the number of double bonds in the fatty acid chain increase, PM emission increases (Figure 8). It is known from CN experiments that more unsaturated fatty acid alkyl ester molecules have a lower ignition quality (low CN) than saturated fatty acid alkyl ester molecules of high CN (Klopfenstein, 1983; Klopfenstein, 1985; Knothe*et al*., 2003).

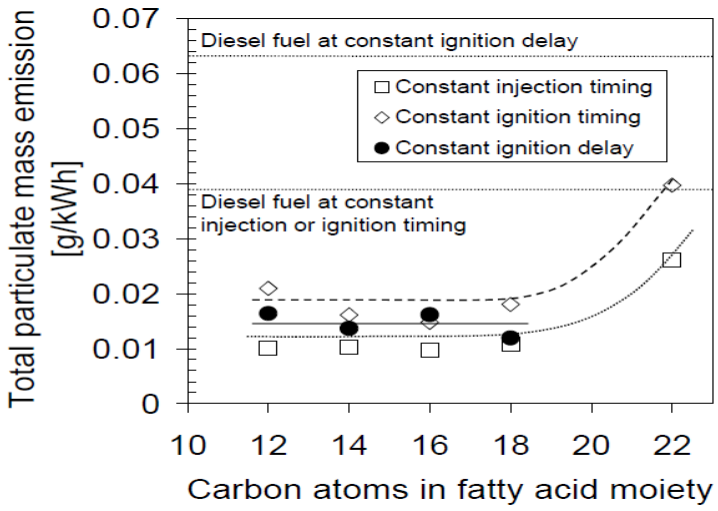

Figure 7: Particulate mass emissions for molecules of different fatty acid chain lengths
Source: Alessandro (2009).

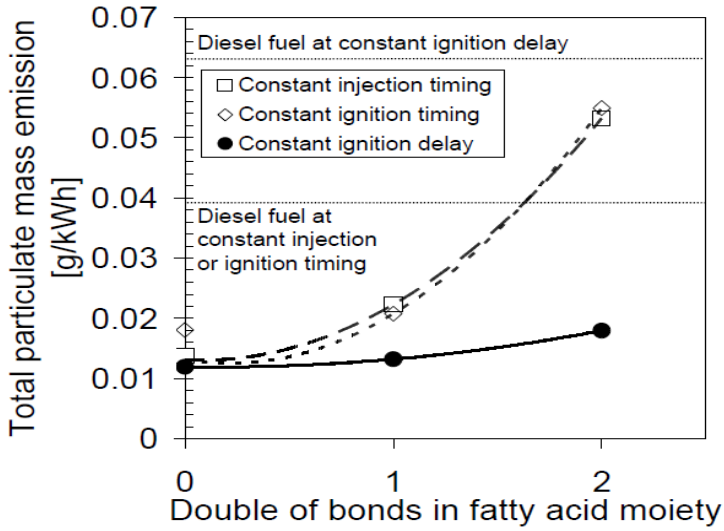

Figure8: Particulate mass emissions for molecules with different number of double bonds
Source: Alessandro (2009)

Also,Ladommatos (1996) showed in an engine experiments that when the start of injection or the start of combustion were held constant that the ignition quality of the fuel expressed as fuel CN, indicated good correlation with the emission of unburned hydrocarbon (UHC). And as CN increases UHC reduces. In the same experiments a progressive increase in smoke emissions was observed as the premixed burn fraction was reduced or as CN is increased (Figure 9). Also, a progressive increase in smoke emissions was observed as the premixed burn fraction was reduced or as CN increases (see Figure 10). The outcome supported earlier prediction that low CN indicted poor ignition quality as well as increase HC emission (Knothe, *et al*., 2003; Pinto *et al*., 2005; Shi *et al*., 2005; Alessandro 2009;Jinlin 2011; Prem*et al*., 2014).

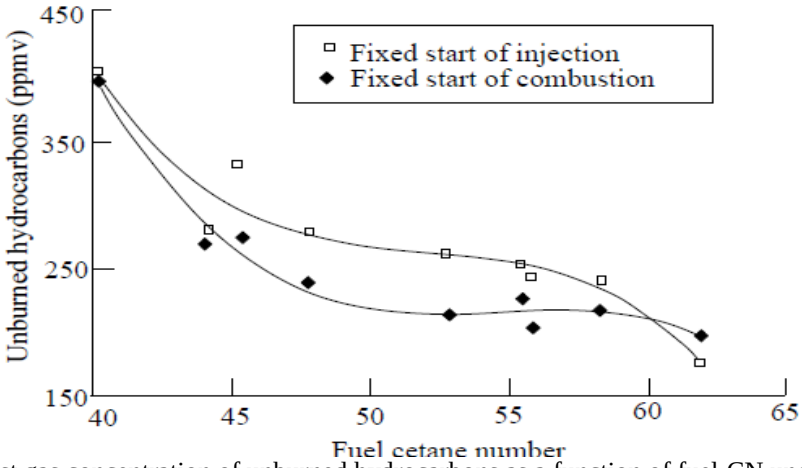

Figure 9: Exhaust gas concentration of unburned hydrocarbons as a function of fuel CN under conditions of fixed start of injection (FSOI) and fixed start of combustion (FSOC).
Source: Ladommatos*et al.* (1996a).

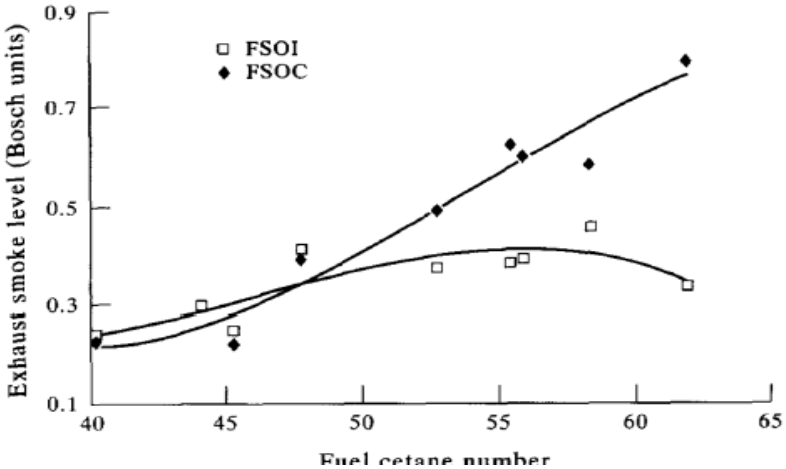

Figure 10: Effect of fuel CN on smoke emissions.
Source: Ladommatos *et al*. (1996a).

Wojciech*et al.* (2011) in an experiment with rapeseed biodiesel affirmed that increasing the CN from 50 to 58 causes considerable (even up to 30%) lowering of the CO and HC emission and lowering NOx by several percent, without significantly affecting the PM emission level. Theycautioned that excessive shortening of the ignition delay period (high CN),may also be disadvantageous because incomplete combustion can occur before the fuel and air are properly mixed. Graboski*et al.* (2003) experimented on the emission of PM in a heavy-duty direct injection diesel engine with electronic unit injection system. They indicated a decrease in fatty acid chain length and an increase in the number of double bonds within the fatty acid moiety of the molecules both resulted in an increase in PM emissions.

VII. EFFECTS OF CETANE ON NOXEMISSION

Many researchers have investigated the effect of CN on NOx emission and confirmed that high CN increasesNOx emission (Agrawal and Das,2001; Canakci and Van Gerpen,2003; Prem*et al*., 2014; Mohd*et al*., 2015; Miłosław, 2016).Knothe (2005) observed that high CNs of fatty compounds and unsaturation in the fatty compounds causes an increase in NOx emissions. The experiment conducted by Rao (2011) on the influence of jatropha biodiesel on emission observed the same trend with Knothe (2005) that biodiesel has higher CN than conventional diesel, therefore shortens ID time and advances the combustion timing which leads to increase NOx emission.

Also, Wang *et al.* (2000) investigated how CN affected NOx emission. They explained that high CN of biodiesel tends to increase peak pressure and temperature due to shortened IDwhich leads to enhanced NOx formation. In the experiment conducted by Karthick*et al.* (2014) on emission characterises of jatropha biodiesel, they observed increased NOxemission (up to 10%) and decrease in smoke because of higher CN. They advocated that higher CN makes combustion occur faster. Jing (2011) also reviewed an experiment where the connection between structure of fatty esters and exhaust emissions was investigated by studying the exhaust emissions caused by enriched fatty acid alkyl esters as fuel. NOx exhaust emissions reportedly increase with increasing unsaturation and decreasing chain length. Particulate emissions, on the other hand, were hardly influenced by the aforementioned structural factors. Also, Zhang and Boehman (2007) indicated that blends having double bonds led to the formation of free radicals that advanced and prompted NOx formation.

Alessandro (2009) reported that longer fatty acid chain length resulted in a shorter ignition delay and produced less NOx during their combustion than shorter chained molecules, but increase in double bond (unsaturation) increase NOx emission. These findings are in agreement with those of Graboski*et al.* (2003) that as the double bond in fatty moiety increase NOx increase. Again a decrease in fatty acid chain length and an increase in the number of double bonds within the fatty acid moiety of the molecules both resulted in an increase in NOx emissions. EPA (2002) conducted analysis to determine the degree to which CN plays a role in the biodiesel/NOx relationship. In the study, relationship between CN and NOxmeasurement was used to generatea regression equationthat predicted the NOx emissions for every fuel in their biodiesel database expressed in equation (6) as:

$$NO_X = e^{\left[(-0.004512)*(CENTUM-45)+0.0001458*{}^{(CNETUM-45)}/_{2}+1.5497034\right]} \quad 6$$

Where: *CETNUM* = cetane number (CN).

The result of the analysis indicated that CN is an important component of the impact that biodiesel has on NOx emissions. Also CN is highly correlated with biodiesel concentrationsuch that the removal of cetane effects on NOx from the NOx measurements leaves little left to be explained by biodiesel concentration. The test showed similar trend between predicted NOx and measured NOx values, the same observation was made by Alessandro (2009) confirming strong correlation between CN and NOx emission(Figure 11)

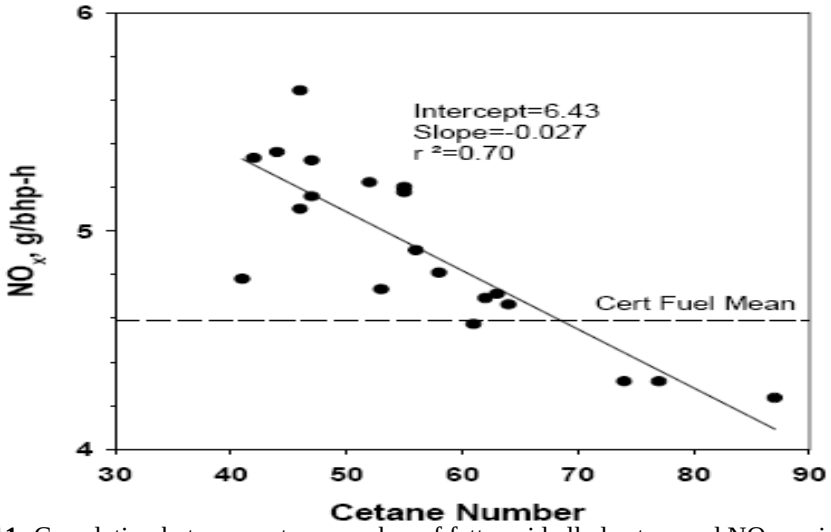

Figure 11: Correlation between cetane number of fatty acid alkyl esters and NOx emission. Source: Alessandro (2009).

Variation in biodieselsCN was one of the reasons given for different levels in NOx emissions in the experimental investigations of Wu *et al.* (2009); Zhu et *al.* (2010); Lapuerta et *al.* (2008); and Lee *et al.* (2005). In another experiment,Mueller *et al.* (2009)explained thatincreasing CN resulted in increased NOx emission. A similar trend was reported when biodiesel B94 and B100 of CN70 and CN 45 each was compared. The blends with CN70 of both blends always showed higher NOx emission than those with CN45 (Palash*et al.*, (2013). However Palash*et al.* (2013) reported that Ban-Weiss *et al.*(2007); Alptekin and Canakci (2008); McCormick *et al.* (2001) in different experiments observed that decreasing the cetane number of biodiesel resulted to increase in NOx emissions. Also,Sabah and Miqdam (2012) reported thatShell and Mercedes-Benz companies in a joined effort investigated the effects of diesel fuel properties (density, distillation range, cetane number and aeronautics content) on exhaust emissions in an advanced European indirect injection (101) passenger car and a modem commercial vehicle direct injection (DI) engine. Their results indicated that the CN and not the total aromatics content accounted for the variation in NOx emissions.Sathiyagnanam*et al.* (2011)added to the explanations for reduced NOx emission due to increased CN. Kirankumar*et al.* (2016) also observed that due to higher CN, ignition delay reduces combustion temperature,therefore aids in reducing NOx emissions since higher combustion temperature is the primary source for NOx increase.

VIII. WAYS OF ACHIEVING A HIGHER CETANE NUMBER

There are two ways to gain a higher CN. The first is to do it during the refining process by using both oil of higher carbon straight chain, saturated bond (no double bond) and alcohol of higher molecular mass. Velmuruganand Gowthamn(2012) reported that refining a high CN diesel fuel usually results in a fuel with a higher API gravity rating and a lower density. Also, higher CN can also be derived through the addition of cetane improver chemistry or additives like 2-ethyl hexyl nitrate, alkyl nitrate, peroxide compounds, and methyl oleate. Generally, these cetane additivesare used in the diesel engine for controlling NOx emissions.

IX. CONCLUSION

Cetane number (CN) of biodiesel is generally higher than those of conventional diesel. CN governs ID.The ignition delay of the fatty acid monoalkyl ester molecules depended strongly on their molecular structure. An increase in the length of the fatty acid moiety, an increase in the saturation of the fatty acid moiety and an increase in the length of the alcohol moiety, all resulted in a decrease of the ignition delay (Alessandro 2009).Higher cetane number indicates shorter ignition delay time, meaning more combustion products, have a longer residence time at high temperatures for complete combustion (Jin 2011).The general trend with biodiesel exhaust emission is reduced CO, HC and PM but increasedNOx as a result of high CN values. Also, the emission of accumulation mode soot particles was positively correlated with the number ofdouble bonds present in the fatty acid moiety of the molecules.Where there are reversed trend, it was explained that higher CN

resulted in a shortened ignition delay period thereby allowing less time for the air/fuel mixing before the premixed burning phase. Consequently, a weaker mixture would be generated and burnt during the premixed burning phase resulting in relatively high CO, HC and PM emission and reduced NOx formation (Prem*et al.*, 2014; Knothe*et al.*, 2003).

REFERENCES

[1]. Agrawal, A.K. and Das, L.M. (2001).Biodiesel development and characterization for use as a fuel in compression ignition engines. Transaction of American Society of Mechanical Engineers, 123:440–7.

[2]. Alessandro, S. (2009). Combustion in a compression ignition engine. Unpublished Ph.D. thesis. Department of Mechanical Engineering. University College London (UCL). July 2009, pp. 1-391.

[3]. Alptekin, E. and Canakci, M. (2008). Determination of the density and the viscosities of biodiesel–diesel fuel blends. *RenewableEnergy* 33:2623–30.

[4]. Bangboye, A. I., and Hansen, A. C. (2008). Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. International Agro-physics, 22 (1): 21-29.

[5]. Ban-Weiss, G.A., Chen, J., Buchholz, B.A., and Dibble, R.W. (2007).A numerical investigation into the anomalous slight NOx increase when burning biodiesel; anew(old) theory. *Fuel Processing Technology*, 88:659–67.

[6]. Barsamin, K. (2009) Methods of Determining Diesel Cetane Number. E-News report. Engineering Consulting and Training Services. Carmegen Engineering inc. www. Carmegen .com.

[7]. Bekal, A. and Babu P. T, (2008). Bio-fuel variants for use in CI engine at design and off-design regimes: An experimental analysis. Fuel Journal, 87; 3550–3561

[8]. Boerlage, G.D.; Broeze, J.J. (1933). "Knock Rating for High-Speed C.I. Engine Fuels." *World Petroleum Congress Proceedings*, (2); p. 271- 277.

[9]. Canakci, M. and Van Gerpen, J.H. (2003). Comparison of engine performance and emissions for petroleum diesel fuel, yellow grease biodiesel, and soybean oil biodiesel. Transaction of American Society of Agricultural Engineers (ASAE). 46(4): 937-944.

[10]. Enaburekhan, J.S., and Bello, S., (2013). Performance of soybean and neem methyl esters as biodiesel on diesel engine. *Academic Journal of Interdisciplinary Studies*, 2(13):47-54.

[11]. Environmental Protection Agency (EPA) (2002). Air and Radiation. A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions. Draft Technical Report EPA420-P-02-001; Pg 5.

[12]. Gabele, P., Karches, W, Ray, W. and Perry, N. (1986). Emissions from a light-duty diesel: ambient temperature and fuel effect, SAE Transaction. 860618, 95(6):455-467.

[13]. Geller, D. P., and Goodrum, J. W., (2004). Effects of specific fatty acid methyl esters on diesel fuel lubricity. *Fuel Journal*. 83 (18): 2351-2356.

[14]. Gordon, R. L., and Mastorakos, E. (*2011).* Autoignition of Monodisperse Biodiesel and Diesel Sprays in Turbulent Flows. *September 11-15.* MCS 7 Chia Laguna, Cagliari, Sardinia, Italy.

[15]. Graboski, M.S., McCormick, R.L., Alleman, T.L.and Herring, A.M. (2003). The Effect of Biodiesel Composition on Emissions from a DDC Series 60 Diesel Engine. National Renewable Energy Laboratory. Report No. NREL/SR-510-31461.

[16]. Guru, M., Koca, A., Can, O., C¸ Inar, C., and Sahin, F. (2010). Biodiesel production from waste chicken fat based sources and evaluation with mg based additive in a diesel engine. *Renewable Energy*. 35:637–43.

[17]. Hannu, J. (2007). Fuel Property Testing: Ignition Quality DieselNet.com.https://www. dieselnet. com/tech/fuel _diesel. php. Copyright © Ecopoint Inc. Revision 2007.07b.

[18]. Harrington, K. J. (1986). Chemical and physical properties of vegetable oil esters and their effect on diesel fuel performance. *Biomass*. 9 (1): 1-17.

[19]. Hossain, F. M., Nabi,M.N.,Rahman, M.M., Zare, A., Rainey,T.J., Stuart, D., Ristovski, Z., and Brown, R. J. (2015). Experimental investigation of the effects of oxygenated fuels on exhaust emissions in a heavy duty diesel engine. Proceedings of the Australian Combustion Symposium. Pp.56-59. The University of Melbourne.

[20]. Hossain, M A., Chowdhury, S M., Islam, M. U., and Alamin H. M. (2012). Analysis of exhaust gas emissions in a diesel engine operating with diesel and biodiesel blends. Proceedings of the 6th International Mechanical Engineering Conference and 14th Annual Paper Meet (6IMEC&14APM) 28-29, IMEC&APM-ABS-000 © IMEC & APM 2012 1 FL-00.

[21]. Hussain, J., Palaniradja, K.,Alagumurthi, N.and Manimaran, R. (2012). Effect of exhaust gas recirculation (egr) on performance and emission characteristics of a three cylinder direct injection compression ignition engine.*Alexandria Engineering Journal* 51:241–247. www.elsevier.com/locate/aej and www.sciencedirect.com.

[22]. Jing, G. (2011) Effects of biodiesel blending on exhaust emissions. Unpublished Ph.D. thesis submitted to the Department of Civil, Environmental, and Architectural Engineering University of Kansas.

[23]. Jinlin, X., Tony, E. G., and Alan, C. H. (2011). Effectof biodiesel on engine performances and emissions. Renewable and Sustainable Energy Reviews, 15:1098–1116.

[24]. Karabektas, M. (2009).The effects of turbocharger on the performance and exhaust emissions of a diesel engine fuelled with biodiesel. *Renewable Energy*, 34:989–93.

[25]. Karabektas, M., Ergen, G., and Hosoz, M. (2008).The effects of preheated cottonseed oil methyl ester on the performance and exhaust emissions of a diesel engine. *Applied Thermal Engineering*; 28(17):2136–43.

[26]. Karthick, D., Dwarakesh, K. and Premnath, R. (2014). Combustion and emission characteristics of jatropha blend as a biodiesel for compression ignition engine with variation of compression ratio. *International Review of Applied Engineering Research*. 4(1):39-46.

[27]. Keskin, A., Guru, M., and Altıparmak, D. (2008).Influence of tall oil biodiesel with mg and mo based fuel additives on diesel engine performance and emission. *Bioresource Technology*, 99:6434–6448.

[28]. Kim, H. and Choi, B. (2010).The effect of biodiesel and bioethanol blended diesel fuel on nanoparticles and exhaust emissions from CRDI diesel engine. Renewable Energy, 35:157–63.

[29]. Kirankumar, S., Apparao, K., and Nagendrababu R., (2016). Effect of exhaust gas recirculation and isobutanol additive on biodiesel fuelled diesel engine for the reduction of NOxemissions. *International Journal of Advanced Science and Technology* (IJAST), 92(3):17-24:

[30]. Klopfenstein, W.E., (1983). Relationship between Cetane Number and Structure for Fatty Acid Esters. In: Vegetable oil as Diesel fuel, US Department of Agriculture, Agricultural Research service, Northern Agricultural Energy Centre, Seminar III, Peoria, ILL., 19th-20th October, pp.104-105.

[31]. Klopfenstein, W.E., (1985). Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels. *Journal of the American Oil Chemists' Society*. 62 (6):1029-1031.
[32]. Knothe G., Matheaus, A.C. and Ryan T.W. III, (2003). *Fuel*, 82; 971.
[33]. Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology*, 86:1059-1070.
[34]. Ladommatos, N. Parsi, M. And Knowles, A. (1996a). The effect of fuel cetane improver on diesel pollutant emissions. *Fuel*. 75(1):8-14.
[35]. Lapuerta, M., Armas, O., and Herreros, J.M. (2008). Emissions from a diesel-biodiesel blend in an automotive diesel engine. *Fuel*. 1:25–31.
[36]. Lee, C.S., Park, S.W. and Kwon, S.I. (2005). An experimental study on the atomization and combustion characteristics of biodiesel-blended fuels. *Energy & Fuels*. 19(5):2201–2208.
[37]. Lertsathapornsuka, V., Pairintrab, R., Aryusukb, K., and Krisnangkura, K. (2008). Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100kWdiesel generator. *Fuel Process Technology*. 89:1330–6.
[38]. Marina, K., Giorgos, F., Giorgos, M., and Leonidas, N. (2008). Effect of biodiesel and bioethanol on exhaust emissions. The European Topic Centre on Air and Climate Change (ETC/ACC) Technical Paper 2008/5.
[39]. McCormick, R.L. Graboski, M.S. Alleman, T.L. Herring, A.M. and Tyson, K.S., (2001). Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environmental Science and Technology*, 35 (9):1742–1747.
[40]. Miłosław, K.(2016). The study on the influence of diesel fuel oxygenates on exhaust emissions. In-tech Alternative Fuels, Technical and Environmental Conditions.pg 41-75. http://dx.doi.org/10.5772/62005.
[41]. Mohd, H., Mat, Y., Rizalman, M., Ahmad, F.Y., Perowansa, P., Talal, Y., andGholamhassan, N. (2015). Effects of exhaust gas recirculation on a diesel engine fuelled with palm-biodiesel. The 7th International Conference on Applied Energy – ICAE2015. *Elsevier*. Energy Procedia 75, 30 – 36. Online at www.sciencedirect.com. doi: 10.1016/j.egypro.2015.07.131.
[42]. Mueller, C.J., Boehman, A.L., Martin, G.C. (2009). An experimental investigation of the origin of increased NOx emissions hen fuelling a heavy-duty compression- ignition engine with soy-biodiesel.SAEPaper:01–1792.
[43]. Nwafor, O., Rice, G., and Ogbonna, A. (2000).Effect of advanced injection timing on the performance of rapeseed oil in diesel engines. *Renewable Energy*, 21(3):433–44.
[44]. Obed, M. A., Talal, Y., Rizalman, M., Nik, R. A. and Abdul, A. A. (2014). Influence of chemical blends on palm oil methyl esters' cold flow properties and fuel characteristics. *Energies. 7*:4364-4380; doi: 10.3390 /en7074364 .www.mdpi.com/journal/energies.
[45]. Palash, S. M., Kalam, M.A., Masjuki, H.H., Masum, B.M., Rizwanul Fattah I.M., and Mofijur, M. (2013) Impacts of biodiesel combustiononNOx emissions and their reduction. *Elsevia*. Renewable and Sustainable Energy Reviews 23; 473–490. http://dx.doi.org/10.1016/j.rser.2013.03.003.www.elsevier.com/locate/rser.
[46]. Pankaj, S., Shelke, N., M. Sakhare, Subhash L., and Kushal S. W. (2016). Analysis of a combustion, performance and emission characteristics of a CNG-B20 fuelled diesel engine under dual fuel mode. *Applied Science Innovations. Carbon – Science and Technology 5:52-59.*
[47]. Pinto, A.C., Guarieiro, L.L.N., Rezende, M.J.C., Ribeiro, N.M., Torres, E.A., and Lopes, W.A. (2005).Biodiesel: an overview. *Journal Brazil Chemical Society*, 16:1313–30.
[48]. Prem K., M.P. Sharma, and Gaurav Dwivedi (2014). Impact of biodiesel on combustion, performance and exhaust emissions of diesel engines.*Journal of Integrated Science and Technology*. 2(2):57-63.
[49]. Ramadhas, A., Muraleedharan, C. and Jayaraj, S. (2005). Performance and emission evaluation of a diesel engine fuelled with methyl esters of rubber seed oil. *Renewable Energy*, 30:1789-800.
[50]. Rao, P.V (2011). Experimental investigations on the influence of properties of jatropha biodiesel on performance, combustion, and emission characteristics of a DI-CI Engine. *World Academy of Science, Engineering and Technology* 51:854-867.
[51]. Refaat, A. (*2009)* Correlation between the chemical structure of biodiesel and its physical properties. *International Journal of Environment Science and Technology*, 6(4):677-694.
[52]. Rehman, A., Pandey, R. K., Dixit, S., and Sarviya, R. M. (2009). Performance and emission evaluation of diesel engine fueled with vegetable oil. *International Journalof Environmental Research*, 3(3):463-470.
[53]. Sabah, T.A. and Miqdam T.C. (2012). Effect of fuel cetane number on multi-cylinders direct injection diesel engine performance and exhaust emissions. *Al-Khwarizmi Engineering Journal*,8(1):65 -75.
[54]. Sathiyagnanam, A.P. and Saravanan, C.G. (2011).Experimental studies on the combustion characteristics and performance of a direct injection engine fueled with biodiesel/diesel blends with SCR. Proceedings of the World Congress on Engineering.WCEVol. III.
[55]. Shahabuddinn, A.M., Liaquat,H.H., Masjuki,M.A., Kalam, M. and Mofijur, A. (2013). Ignition DELAY, combustion and emission characteristics of diesel engine fueled with biodiesel. *Renewable and Sustainable Energy Reviews*, 21:623–632.
[56]. Shi, X., Yu, Y., He, H., Shuai, S., Wang, J. and Li, R. (2005). Emission characteristics using methyl soyate–ethanol–diesel fuel blends on a diesel engine. *Fuel*, 84:1543–9.
[57]. Ullman, T. L., Mason, R. L. and Montalvo, D.A. (1990). Effects of fuel aromatics, cetane number and cetane improver on emissions from a 1991 prototype heavy duty diesel engine, Society of Agricultural Engineers paper No. 9021 71.
[58]. Van-Gerpen, J. H. (1996).Cetane number testing of biodiesel. Proceedings of the 3rd Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources. American Society of Agricultural Engineers (ASAE), September 15-17.
[59]. Velmurugan, K. and Gowthamn, S. (2012). Effect of cetane improver additives on emissions. International *Journal of Modern Engineering Research*, 2(5):3372-3375.
[60]. Wang, W., Lyons, D., Clark, N., Gautam, M. and Norton, P.(2000). Emissions from nine heavy trucks fuelled by diesel and biodiesel blend without engine modification. *Environmental Science and Technology*, 34:933–9.
[61]. Wojciech, G., Andrzej, Z., and Anna, B. (2011). Properties of the rapeseed oil methyl esters and comparing them with the diesel oil properties. *Journal of KONES Power train and Transport*, 18(4):121-127.
[62]. Wu, F., Wang, J., Chen, W. and Shuai, S. (2009). A study on emission performance of a diesel engine fuelled with Five Typical Methyl Ester Biodiesels. *Atmospheric Environment*, 43:1481–1485.
[63]. Yanowitz, J., Ratcliff, M.A., McCormick, R.L., and Taylor, J.D. (2014). Compendium of experimental cetane. National renewable energy laboratory. Technical Report. NREL/TP-5400-61693. • www.nrel.gov.
[64]. Zhang, Y. and Boehman, A.L. (2007). Impact of biodiesel on NOx emissions in a common rail direct injection diesel engine. *Energy and Fuels*. 21:2003–12.
[65]. Zhu, L., Zhang, W., Liu, W. and Huang, Z. (2010). Experimental study on particulate and NOxemissions of a diesel engine fuelled with ultra-low sulphur diesel, RME-diesel blends and PME-diesel blends. *Science Total Environment*; 408:1050–8.