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Content

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Triacylglyceride's Transesterification for Biodiesel: a Review

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Abstract

Biodiesel can be produced from various oils or TAG's by transesterification in the presence of different catalyst. Biodiesel can be used either in pure form or blended form can be directly used in diesel engine without any modification or little modification. This review presents the transesterification of oil using different catalyst and their mechanism. Homogeneous and heterogeneous catalysts are discussed along with their advantages and disadvantages. This review also gives insight on the microwave heating of reactions and traditional method of heating of reactions. Apart from this use of enzyme based catalyst and current status is explained. Now a day's nano-size catalyst also gains much attention due to large surface contact area.

Keywords- *Transesterification; Catalyst; Enzyme; Nanoparticle catalyst.*

Introduction

There are many feedstock's from which biodiesel is obtained. This oil cannot be directly used to run engine due to high viscosity and low volatility which leads to injector coking and engine deposit [1,2]. However this problem is eliminated by transesterification of oil to alkyl ester [1, 3].

Transesterification is also called alcoholysis. Transesterification is reversible reaction in which triglycerides are converted to di-glycerides and to mono-glycerides which finally gives glycerol. Biodiesel floats at the top while glycerol sinks to the bottom which is separated easily [4]. In transesterification methanol

and ethanol is mainly used as alcohol due to low cost. However octanol, propanol, butanol and tert butanol can also be used but their cost is higher as compared to methanol and ethanol [5,6,7,8]. If methanol is used in reaction then process is called methanolysis. General equation for transesterification is represented as in fig. 1 [9].

This reaction generally takes place in presence of catalyst which may be acidic or basic in nature as alcohol is scarcely soluble in oil, so catalyst increase the solubility, thus accelerates the reaction [4]. The transesterification process removes the glycerin, so viscosity decreases but heating value and cetane number does not change [10].

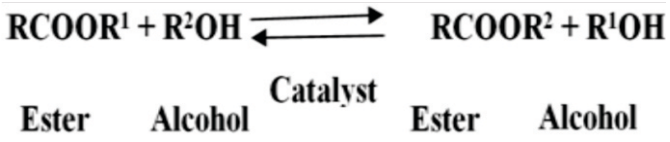


Figure1: Transesterification reaction

1.1. Kinetics of transesterification reaction

The oil from which biodiesel is produced is known as triglyceride (TAG). TAGs are formed by covalent bonding of carboxylic acid with alcohol. In this context, TAG is an ester formed by combining of three molecules of fatty acids covalently bonded with glycerol molecule [11]. Fatty acid has carboxylic group while glycerol has three hydroxyl group which while combining form ester or TAGs. Transesterificationis a chemical process in which carboxylic acid ester is converted into different carboxylic acid esters.

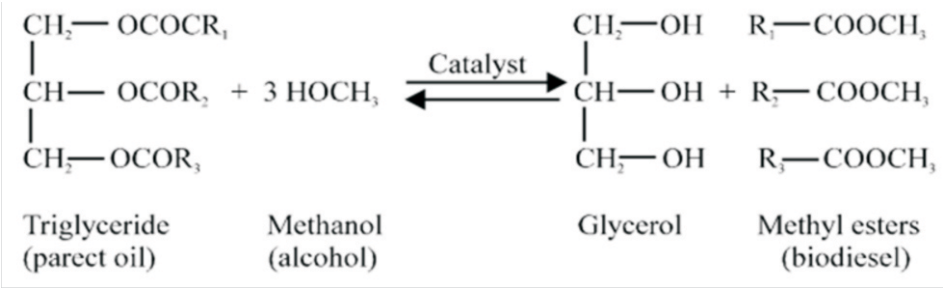


Figure 2 transesterification reaction

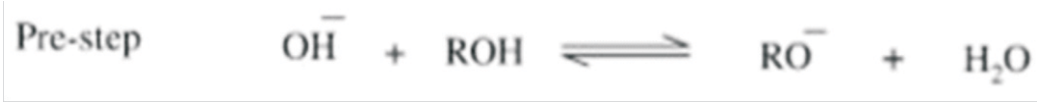
2. Base-Catalysed Transesterification

Base catalyst are mostly used for transesterification of vegetable oils [12,13,14,15,16]. When the tryglyceride contains free fatty acids or excess amount of water then acid catalyst are used to reduce the soap formation [13,16, 17]. Base catalyzed transesterification reaction is 4000 times faster then acid catalyzed reaction but it is used only if trygleceride contains less then 2% free fatty acids [18]. Sodium and potassium hydroxide are mostly used for industrial purpose.

2.1. Mechanism of Base catalyzed Transesterification

The transesterification using base catalyst involves four step pre step or first step in which base reacts with alcohol and form protonated catalyst and an alkoxide. In the next step carbonyl group of oil is attacked by nucleophilic and forms intermediate [19, 20,12]. In third step alkyl ester and anion of diglyceride are formed. In fourth step the catalyst deprotonates, thus regenerating the base which again reacts with second molecule of alcohol and starts another cycle.

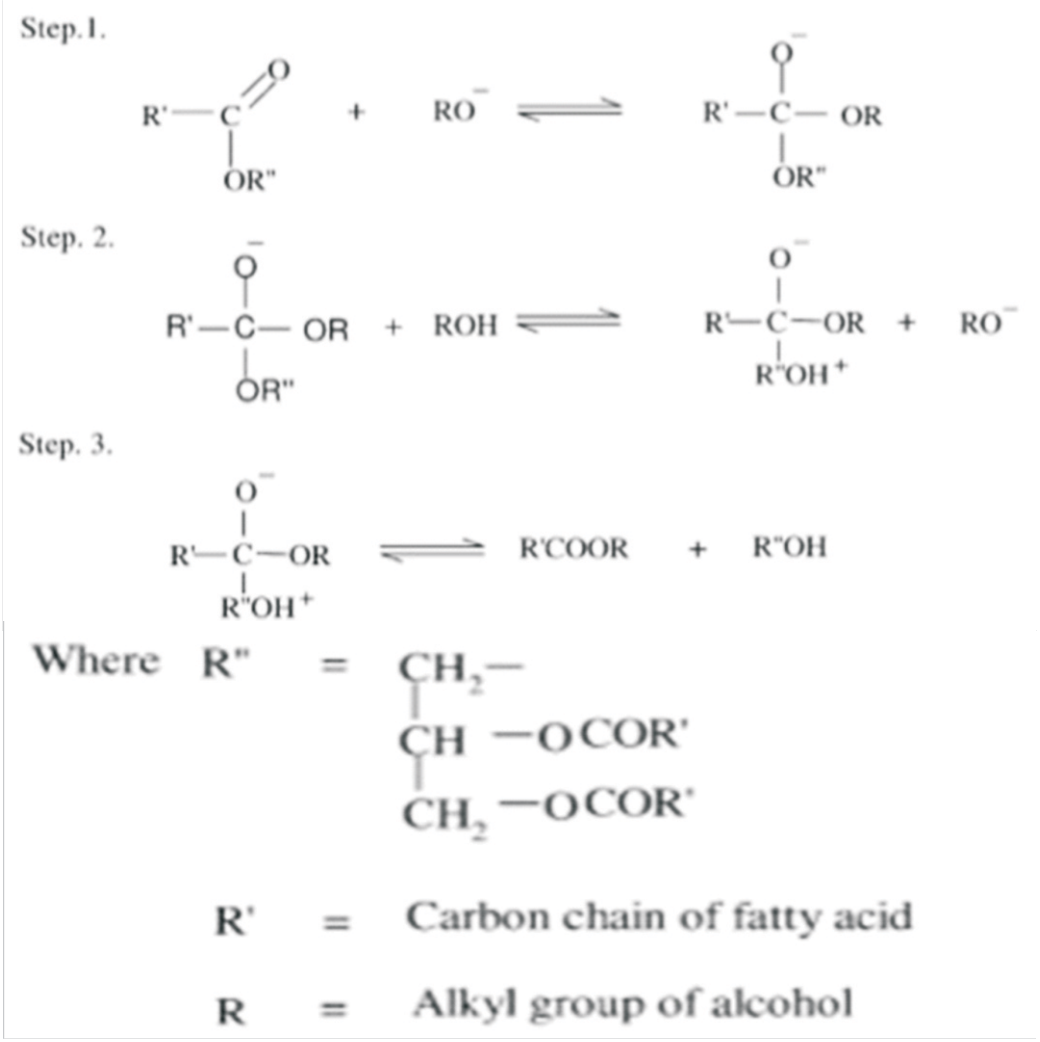
Base catalyst are mostly used because reaction takes place at low temperature and pressure that is 60C° and 20 psi and obtain high yield about 98%. However there are some shortcomings it requires high energy, to separate the catalyst from the media after transesterification pro-reaction treatment is required, difficult to recover glycerol after the reaction moreover it forms soap with free fatty acids.



2.2. Factors affecting base catalyzed transesterification.

Effect of alcohol to oil molar ratio: the yield of methyl esters generally depends upon methanol to triglyceride molar ratio. Theoretically three moles of methanol are required per mole of oil for transesterification. A vegetable oil [21] studied the amount of alcohol required for transesterification of vegetable oil in terms of alcohol to oil molar ratio. Shazia sultana [22] studied transesterification on five different molar ratios in the range 2:1 to 10:1 and obtained maximum yield 92%

with 6:1 methanol to oil molar ratio. On further increase in methanol to oil molar ratio the ester yield decreases.



Encinar J.M et al [23] studied different ethanol to oil molar ratio between range 3:1 to 15:1 for the transesterification of cynarer oil and reported that reaction is incomplete when molar ratio is less than 6:1. The yield of ester increases as the molar ratio increased upto 12:1 and obtained optimum value at 9:1. However many authors reported that [24,25] with increase in methanol to oil molar ratio the yield decreases, for

instance, Lu et al [24] worked on different molar ratio ranges from 1:1 to 1:10 and reported that the maximum yield is obtained at 1:1 and this may be due to inhibitory effect of alcohol on lipase activity.
Similarly Li et al [25] given same trend that with increase in molar ratio yield decreases, the achieved 95% yield in 12 hour at molar ratio 4:1.

2.3 Effect of Catalyst Concentration
Mostly alkaline, acid and enzyme catalyst are used. If the oil contains high free fatty acids and large quantity of water then acid catalyst is used for transesterification. Sultana Shazia [22] studied the effect of NaOH concentration between the range of 0.1-0.9 wt% and obtained that yield increases with increase in catalyst concentration from 0.1-0.5%. The yield decreases with further increase in NaOH concentration and reduced to 50% with 1.5% NaOH concentration. This is because with increase in the concentration of catalyst, soap formation will take place and reduce the yield with increase in viscosity. Ma F et al [27] studied the effect of NaOH and NaoME concentration and found that at 3% and 5% w/w of catalyst to beef tallow oil maximum yield is obtained.

3. Acid-Catalyzed Transesterification
The acid catalyzed transesterification does not gain much popularity because it is 4000 times slower than the alkali catalyzed reactions [18]. Its performance does not affected by the presence of free fatty acids and can catalyze simultaneously both esterification and trans-esterification. Acid catalyst can produce biodiesel from low cost feed stock having high free fatty acid FFA. The transesterification of triglyceride consist of three reversible reactions. Acid catalyzed transesterification mechanism is shown in fig for monoglyceride. Carbonyl group protonation leads to carbocation which forms tetrahedral intermediate after the nucleophilic attack of alcohol. The glycerol is separated and forms new ester. These reactions should be carried in the absence of water because carbocation reacts with water to form carboxylic acids.

4. Catalyst for transesterification Process
For transesterification following catalyst are investigated, heterogenous, enzymatic and homogenous or alkali catalyst like potassium and sodium hydroxide are mostly used in industrial

transesterification because they promote reaction at low temperature also [28].

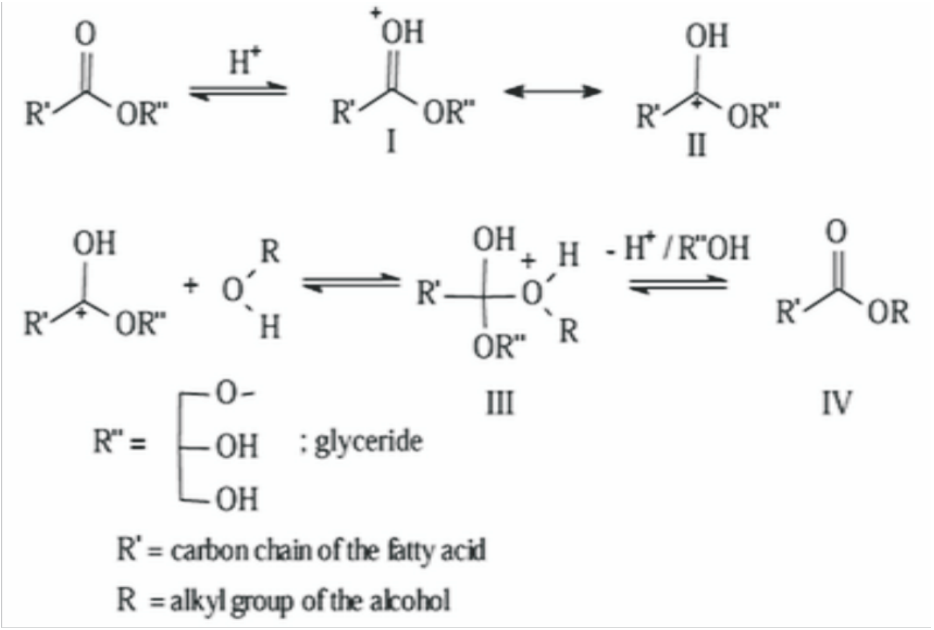


Figure 4. Mechanism of acid catalyzed reaction.

4.1. Homogenous Catalyst

Homogeneous catalysts are further divided as homogeneous acids and homogeneous base catalys Homogeneous base catalysts are commonly used for transesterification of triglyceride. Homogeneous base catalyst such as carbonates [29], alkaline metal hydroxide [30,31] and alkoxides [17, 32] are most commonly used [28] the alkoxide are more difficult to handle then hydroxide because alkoxide are hygroscopic in nature. Alkoxide does not form soap from triglyceride saponification due to the presence of hydroxide ion which act as an impurity in alkoxide [28]. While using alkaline catalyst the free fatty acid content should not increase 0.5% by wt. otherwise soap formation will takes place which hampers the production of biodiesel. Various authors reported that 90% yield is obtained by using potassium hydroxide and boiler ashes in the methanolysis and ethanolysis of coconut and palm oil [3323, 34, 35]. Ma et. al. [27] found that alkaline

catalyst Naoh perform better than NaoMe. However to obtain higher yield the concentration of naome is slightly higher as compared to Naoh Ma et. al. [27]. Singh et al. [36] studied about alkaline catalyst (NaoH, KoH, KoMe and NaoMe) and found that better yield is obtained by potassium based catalyst as compared to sodium based catalyst. Where methoxide based catalyst produces higher yield compared to hydroxide based catalyst.

4.2. Homogeneous Acid Catalyst

For the transesterification of free fatty acid (FFAs) h**o**mogeneous acid catalyst are more effective as compared to base catalyst. Acid catlysed reactions proceed 4000 times slower than the base catalyzed reaction[15]. However acid catalyzed reactions have lower moisture sensitivity as well as non-appearance of soap formation. Acid catalysts are used where oil has higher FFAS [28]. If base catalyst are used it will form soap. Acid catalyzed reactions are two stage processes, in first stage esterification takes place in the presence of acid catalyst while in the second stage reaction takes place in the presence of base catalyst.
The acid catalyst mostly used are, sulphonic acid, organic sulfonic acid, hydrochloric acid, and phoshphoric acid. Freedman et al. [32] uses sulphuric acid as catalyst with alcohol oil ratio 30:1 and found that to obtain 90% yield reaction took 50h to complete at 65℃. Zullaikah et. al. [37] uses sulphuric acid as catalyst for the transesterification of rice bran oil between temperature range of 60-80℃.

4.3. Heterogeneous Catalyst

It is difficult to separate homogeneous catalyst from the reaction mixture so heterogeneous catalysts are developed. Heterogeneous catalyst. heterogeneous catalyst are advantageous because they does not form soap through saponification of triglyceride and eliminate corrosion problems and reaction requires high temperature and pressure. However there are some limitations like, they have poor performance compared to homogeneous catalyst, and due to less surface contact catalyst does not participate effectively in reaction so catalyst must be in porous state. The surface of heterogeneous catalyst must be hydrophobic in nature so that it adsorb triglyceride and to avoid adsorption of polar by products like water and glycerol on surface. Solid catalyst which are mostly used are, alkaline earth oxide, solid organic

base, basic oxides supported, basic zeolite, insoluble metal salt and hydroxide, basic metal oxide, hydrotolerite and hetropolyacids [38].

4.3.1 Alkaline Earth Oxide

Ca and Mg are alkaline earth metals which are most widely used as heterogeneous base catalyst. Gryglewicz [31] found that alkali earth metal oxides sucessfuly catalyzed the transesterification reaction. Alkaline earth oxides are basic due to M^{2+} and O^{2-} ion pairs [39]. Various authors reported the use of Cao as catalyst for the transesterification of sunflower, and rapeseed oil with methanol [40, 41]. Moreover, strontium oxide, Cao, Mgo also investigated as catalyst for transesterification with high basicity [42, 43, 44].

Martyanov and Sayari [45] used calcium methoxide as catalyst for the transesterification of triglyceride and found that initially reaction is slower as compared to homogeneous sodium methoxide and magnesium methoxide, but at later stage the rate of reaction is higher than magnesium methoxide. Alkaline earth metal oxides assimilate with metal oxide and form composite oxide [46] which can be used as solid base catalyst for transesterification. Composite oxides are more stable and easy to separate from the reaction media.

4.3.2. Acid Zeolite

Zeolites are most widely used as solid acid catalyst for transesterification of oil and made hydrophobic by elimination of water of hydration. Shu et al, [47] uses La/Zeolite beta catalyst for the batch transesterification of soybean oil and found that La/Zeolite base catalyst have higher conversion rate than zeolite beta heterogeneous acid catalyst used in biodiesel production are mostly mesoporous [48, 49]. Subsume of microporous H-β- Zeolite with secondary mesoporosity create a heterogeneous solid catalyst which accelerates microalgae transesterification by reducing the diffusion barriers [50, 51] uses zeolite catalyst for the transesterification of waste cooking oil and found that yield is independent of porosity of zeolite and found that yield increases with increase in strength of the acid**.**

4.3.3. **Hetropolyacids**

Hetropolyacids attains much attention due to its superacidic nature (PK H^{+}> 12) and porous structure. They are highly soluble in polar media in their native form which make their

contribution in reaction as homogeneous catalyst [52]. Chai et al, [53] uses heterogeneous catalyst ($CS_{2.5}H_{0.5}PW_{12}O_{40}$) for transesterification of eruca sativa gars oil and obtained the same result as by using sodium hydroxide or sulphuric acid with one advantage of easy separation of catalyst from media and its reuse. Cao et al [54] use the hetroppolyacids ($H_{35}PW_{12}O_{40}.6H_2O$) catalyst for transesterification of waste cooking oil. In 10h 87% yield is obtained using hexhydrate catalyst. The catalyst would be separated easily and was reused many times.

5. Microwave Irradiation Effect on Biodiesel Production

Traditionally organic reactions are heated by various equipments such as sand bath, heating jackets and oil baths. These techniques are not effective because they are slower and temperature gradient took place. But now a days microwave dielectric heating is preferred in microwave heating radiation passes the wall and only heat the solvent and reactants without heating the vessel [55].

Patil et. al., [56] used micro-algal oil to produce biodiesel by transesterification by heating with microwave radiation and observed that microwave irradiation effect the reaction in two way 1. reaction is boosted by thermal effect. 2. Vaporization of methanol due to strong microwave radiation. Ma et al, [57] observed that microwave heating reduce energy and reaction time due to volumetric heating.Ma et al, [57] produced biodiesel by transesterification of micro-algal oil in the presence of KOH by conventional heating and microwave heating method and find that with conventional heating system reaction completes in 210 minute while with microwave heating reaction completes in 5 min, obtained 96.54% conversion using KOH 1% wt, 1:8 oil to methanol at 65℃.

6. Nanoparticle Catalyst In Transesterification

For the conversion of triglyceride to methyl esters transesterification takes place in the presence of catalyst. Catalysts used are either base catalyst or acid catalyst. Base catalyzed reactions are much faster than that by acid catalyzed reaction. However basic catalyst have some drawbacks such as loss of catalyst, some catalyst remain in the biodiesel does not separated. To overcome this drawback heterogeneous catalyst are used but

require long reaction time and large volume. Therefore, to improve the conversion of free fatty acid, lots of efforts are done to produce catalyst with high surface area. Highest methyl esters can be produced by catalyst with high surface area [58]. Many authors investigated that Nano sized catalyst have large contact area. For instance, Wang et. al., [59] produced biodiesel from waste cooking oil in the presence of nano-sized catalyst (Aluminum dode catungs to phosphate AIPW) and observed that ≈ 96% conversion was achieved at 55°C due to large surface area of nano paticle.

6.1. CaO/ MgO catalyst

Calcium oxide is heterogeneous base catalyst mostly used for transesterification reaction. It has many advantages, such as easy availability, higher activity, reusability, low cost and mild reaction condition. Pretreatment temperature range between 700-1000 K is used to remove water and CO_2 which is adsorbed on the surface of CaO [60]. Most of the catalyst has adverse effect on yield of methyl ester in the presence of water. However CaO catalyst performs well in the presence of water, it forms methoxide ion in the presence of methanol which is highly active. Mechanism of transesterification with CaO as catalyst is given in fig [61].

As shown in equation 1, Ca^{2+} extracts OHand O_2^- extracts $H^+$from water so they are easily extracted by reactants during chemical reaction. As shown in equation 2, methoxide anion and HO_2 forms when OH extracts H^+methanol. In equation 3 again O^{-2} extract H^+ and form surface methoxide anion. If water exceed by 2.8 wt% of oil it hydrolyze the methyl esters and forms fatty acid and methanol. Liu et. al., [61] obtained 95% yield at temperature 65° C by using CaO catalyst. Hsiao [75] used nano powder CaO as catalyst and obtained 96.6% yield at 1:6 oil to methanol ratio, reaction time 1 hour, 338 K temperature and 3 wt% catalyst.

Due to easy preparation and low cost researcher focus attention on MgO and CaO catalyst. Huaping [62] obtained 93% yield using CaO as catalyst. Di serio [63] achieved 92% yield by using MgO as catalyst. Dossin [64] use MgO as catalyst in batch work reactor and found that satisfactorily at ambient condition. Magnesium oxide is identified as good homogeneous catalyst for transesterification of ethyl acetate with methanol [64].

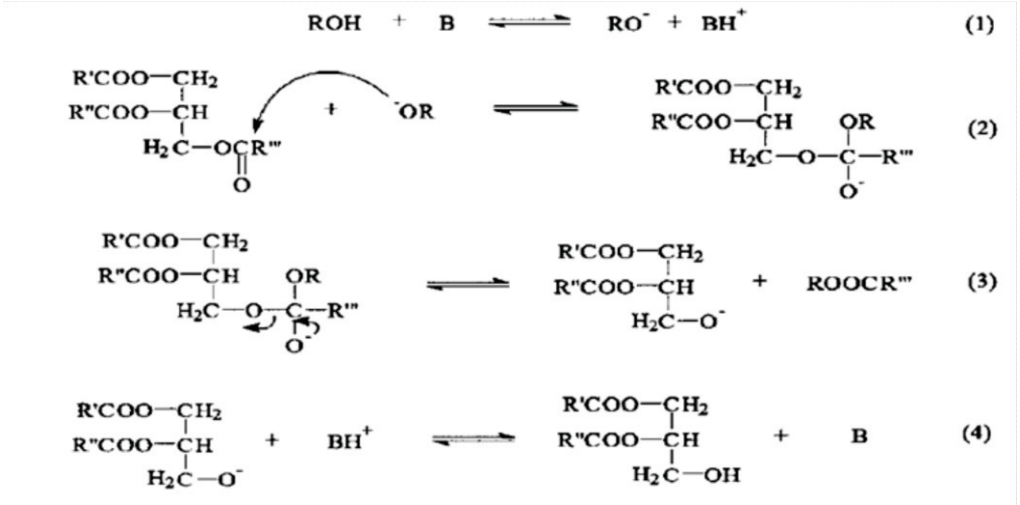


Fig 5. Transesterification mechanism in the presence of water using CaO as catalyst.

6.2. CaOZnO Catalyst

The combination of Cao and ZnO (CaOZnO) catalyst in palm kernel oil **transesterification is studied**. The mixture of CaO and ZnO has small particle size which result in large surface contact area as compared to individual oxides. Ngamcharussrivchai [53] used CaOZnO catalyst with Ca/Zn ratio 0.25 for the transesterification of palm kernel oil and obtained greater than 94% yield at reaction temperature 60C°, methanol to oil ratio 30 and reaction time 60 minute. CaOZnO catalyst is used for the transesterification of sun flower seed oil and 90% yield is obtained [65]. The CaO and ZnO are synthesized by Co-precipitation method or impregnation method. Ngamcharussrivchai [53] found that the catalyst synthesized by the co precipitation method result in higher yield (94.2%) compared to impregnation method (90%). The literature shows that the activity of reaction depends on Ca to Zn atomic ratio it is synthesized between ratio, from ¼ to 4. At atomic ratio of 0.25 the CaOZnO catalyst produce 93.5% of esters which is larger as compared to other atomic ratio.

7. Enzyme catalyzed transesterification

The problem related to conventional catalytic process, like removal of catalyst, treat large amount of waste waterand high energy requirement are solved by using enzymes. Enzyme do not form any soap like alkaline catalyst and without the need of washing they esterify both FFA and TAG in single step. These are biological catalyst and can catalyze different chemical reactions. They can be either used in free or immobilized form in transesterification that leads to the production of biodiesel [66]. A wide range of enzymes such as lipase has been used for esterification [67]. Lipase from fungi and bacteria are mostly used for process and they belong to group of hydrolytic enzymes which is also known as hydrolases.

The lipase catalyzed reaction is classified as [68].

1. hydrolysis 2. Synthesis a) esterification b) transesterification.

1) Hydrolysis

$R^1COOR^2 + H_2O \rightleftharpoons {}^1RCOOH + R^2OH$

Esterication

$R^1COOH + R^2OH \rightleftharpoons {}^1RCO^2OR + H_2O$

Transesterification

Alcoholysis

$R^1COOR^2 \rightleftharpoons + R^3OH$

$R^1COOR^3 + R^2OH$

Acidolysis

$R^1COOR^2 \rightleftharpoons + R^2COOH$

$R^3COOR^2 + R^1COOH$

7.1.Immobilization of lipase

Immobilization of lipase is the state of arrest of the enzyme in region [69]. Immobilization provide number of benefits such as enzyme reuse, easy separation of product from enzyme [70]. Many other properties are also improved such as chemical, thermal and mechanical properties making them to use in harsher environmental condition [71,72].Salah [73]obtained 25% conversion with immobilized lipase and 3% conversion with free lipase while butanolysis of acetic acid. General technique used for immobilization are 1). Adsorption 2) Entrapment 3) Cross linking 4) Encapsulation . Adsorption is simplest method; in this enzymes are attached to the surface by combination of Vander wall or electrostatic forces.

7.2. Effect of presence and absence of solvent enzyme based transesterification

Using enzyme as catalyst for biodiesel production of oil is tried in the presence and absence of solvent. Nelson [74]done methanolysis of tallow oil using hexane as solvent in the presence of Mucormehei lipase and obtained 77.8% yield. But many workers favours solvent free reactions. Furthermore toxicity and inflammability of solvents, prevent the use of solvent enzyme based transesterification. Oznur [76] done transesterification of cotton seed oil using immobilized lipase and obtained 92% of yield in a solvent free medium.

Conclusion

This review includes the transesterification of oil using alkali and acid catalyst. The effect of parameters such as, molar ratio, catalyst concentration and methanol to oil ratio are discussed. Selection of homogeneous, heterogeneous and enzymatic catalyst is explained. Homogeneous base catalysts are commonly used for industrial purposes whereas heterogeneous and homogeneous acid catalysts have lesser use. Homogeneous acid and base catalyst require excess alcohol. Homogeneous catalyst is mainly used for batch mode process, followed by catalyst separation. Moreover homogeneous alkali catalysts are sensitive to free fatty acids and HO_2 results in saponification. The feed stock having FFA require acid and base catalyst which is two stage process in which acid catalyst are firstly used and then removed before the use of alkaline catalyst. However the use of acid catalyst increases the corrosiveness. Now a days much more attention is focused on enzyme based catalyst instead of chemical catalyst because enzyme based catalytic reaction proceed at moderate conditions, require low alcohol to oil ratio, and easy product recovery. Use of nano- particle catalyst and heating reactions with the help of microwave is discussed.

References

[1] Perkins LA, Peterson CL, Durability testing of transesterified winter rape oil (Brassica napus L.) as fuel in

small bore, multi-cylinder, DI, CI engines, *Society of Automotive Engineers*, *Warrendale* (1991).

[2] Scholl KW, Sorenson SC, Combustion of Soybean oil methyl ester in a direct injection diesel engine, *Society of Automotive Engineers, Warrendale* (1993).

[3] Zhang Q, Feldman M, Peterson C, Diesel engine durability when fueled with methyl ester of winter Rapeseed oil, *American Society of Agricultural Engineers, Washington DC* (1988).

[4] Atabani AE, Silitonga AS, Badruddina Irfan Anjum, Mahliaa TMI, Masjukia HH, Mekhilefd S, A comprehensive review on biodiesel as an alternative energy resource andits characteristics, *Renewable and Sustainable Energy Reviews*, 16, 2070–2093 (2012).

[5] Shahid EM, Jamal J, Production of biodiesel: a technical review, *Renew Sustain Energy Rev*, 15(9):4732–45 (2011).

[6] Balat M, Balat H, Progress in biodiesel processing, *Appl Energy*, 87(6):1815–35 (2010).

[7] Demirbas AH, Demirbas I Importance of rural bioenergy for developing countries, *Energy Convers Manage*, 48(8):2386–98, (2007).

[8] Fukuda H, Kondo A, Noda H, Biodiesel fuel production by transesterification of oils, *J Biosci Bioeng*, 92(5):405–16 (2001).

[9] Meher LC, Sagar D Vidya, Naik SN, Technical aspects of biodiesel production by transesterification - a review, *Renewable and Sustainable Energy Reviews*, xx (xxxx) 1-21 (2004).

[10] Awolu Olugbenga Olufemi and Layokun Stephen Kolawole, Optimization of two-step transesterification production of biodiesel from neem (Azadirachta indica) oil,*International Journal of Energy and Environmental Engineering*, 4:39 (2013).

[11] Gaurav Kumar, Srivastava Richa and Singh Ram, Exploring

biodiesel: chemistry, biochemistry and microalgal source, *International journal of green energy*, 10: 1-22 (2013).

[12] Meher LC, Sagar D Vidya, Naik SN, *Renew. Sustain. Energy Rev.*, 10, 248–268 (2006).

[13] Kaeida M, Samukawa T, Ban K, Kondo A, Shimada Y, Noda H, Nomoto F, Othsuka K, Yzumoto E, Fukuda H, *J. Biosci. Bioeng.*, 88, 627-631 (1999).

[14] Antolin G, Tinaut FV, Briceno Y, Perez C, Ramirez Al, *Biores. Technol.*, 83, 111-114 (2002).

[15] Srivastava A, Prasad R, *Renewable Sustainable Energy Rev.*, 4, 111-133 (2000).

[16] Zhang Y, Dube MA, Mclean DD, Kates M, *Bioresour. Technol.*, 89, 1–16 (2003).

[17] Freedman B, Pryde EH, Mounts TL, *J. Am. Oil Chem. Soc.*, 61, 1638 (1984).

[18] Sharma YC, Singh B, *Fuel*, doi:10.1016/j.fuel.2007.08.00 1 (2007).

[19] Taft RW, Newman MS and Verhoek FH, *J Am Chem Soc.*, 72, 4511 (1947).

[20] Guthrie JP, *J Am Chem Soc*., 113, 3941 (1991).

[21] Prafulla D and Deng PS, Optimization of biodiesel production from edible and non-edible vegetable oils, *Fuel* 88:1302–6 (2009).

[22] Sultana Shazia, Khalid Aneela, Ahmad Mushtaq, Zuhairi Ahmad Abdullah, Teong Lee Keat, Zafar Muhammad, and Hassan Fayyaz ul, The production, optimization, and characterization of biodiesel from a novel source: Sinapis alba L., International Journal of Green Energy, 11: 280–291 (2014).

[23] Encinar J M, Gonzalez J F, Rodriguez J J and Tejedor A, *Energy Fuels*, 16, 443-450 (2002).

[24] Lu J, Deng L, Zhao R, Zhang R, Wang F, Tan T, Pretreatment of immobilized Candida sp. 99–125 lipase to improve its methanol tolerance for biodiesel production, *J Mol Catal B: Enzym*, 62(1): 5–18 (2010)

[25] Bousquet-Dubouch MP, Graber M, Sousa N, Lamare S,

Legoy MD, Alcoholysis catalyzed by Candida antarctica lipase B in a gas/solid system obeys a Ping Pong Bi Bi mechanism with competitive inhibition by the alcohol substrate and water, *Biochim Biophys Acta Protein Struct Mol Enzymol*, 1550(1): 90–99 (2001).

[26] Li L, Du W, Liu D, Wang L, Li Z, Lipase-catalyzed transesterification of rapeseed oils for biodiesel production with a novel organic solvent as the reaction medium, *J Mol Catal B: Enzym*, 43(1–4):58–62 (2006).

[27] Ma F, Clements L D, Hanna M A, *Trans. Am. Soc. Agr. Eng.*, 41, 1261 (1998).

[28] Sivasamy Arumugam, Cheah Kien Yoo, Fornasiero Paolo, Kemausuor Francis, Zinoviev Sergey, and Miertus Stanislav, Catalytic applications in the production of biodiesel from vegetable oils, *ChemSusChem*, 2, 278 – 300 (2009).

[29] Arzamendi G, Arguinarena E, Campo I, Zabala S, Gandia L M, *Catal. Today*, 133–135, 305 (2008).

[30] Rashid U, Anwar F, Moser B R, Ashraf S, *Biomass Bioenergy*, 32, 1202 (2008).

[31] Gryglewicz S, *Bioresour. Technol*., 70, 249 (1999).

[32] Freedman B, Butterfield RO, Pryde EH, *J. Am. Oil Chem. Soc.*, 63, 1375 (1986).

[33] Graille J, Lozano P, Pioch D and Geneste P, *Oleagineux*, 41, 457-464 (1986).

[34] Ejikeme P M, Waste vegetable oils as alternative to diesel fuel in compression ignition engines, *Book of Proceedings, International Workshop on Renewable Energy for Sustainable Development in Africa*, NCERD, UNN (2007).

[35] Ejikeme PM, Egbuonu CAC and Anyaogu ID, Fatty Acid Methyl Esters of Melon Seed Oil, Characterization for Potential Fuel Applications, *Book of Proceedings, Coalcity Chem*, Enugu-Nigeria (2008),

[36] Singh AP, He BB, Thompson JC, Gerpen JH Van, *Appl. Eng. Agr.*, 22, 597 (2006).

[37] Zullaikah S, Lai CC, Vali SR, Ju YH, *Bioresour. Technol.*, 96, 1889 (2005).

[38] Lee Adam F, Bennett James A, Manayil Jinesh C and Wilson Karen, Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification, *Chem. Soc. Rev.*, 43, 7887 (2014).

[39] Hattori H, *Chem. Rev.*, 95, 537–558 (1995).

[40] Peterson GR and Scarrah WP, *J. Am. Oil Chem. Soc.*, 61, 1593–1597 (1984).

[41] Verziu M, Coman SM, Richards R and Parvulescu VI, *Catal. Today*, 167, 64–70 (2011).

[42] MacLeod CS, Harvey AP, Lee AF and Wilson K, *Chem. Eng. J.*, 135, 63–70 (2008).

[43] Montero J, Wilson K and Lee A, *Top. Catal.*, 53, 737–745 (2010).

[44] Watkins RS, Lee AF and Wilson K, *Green Chem.*, 6, 335–340 (2004).

[45] Martyanov IN, Sayari A, *Appl. Catal. A: Gen.*, 339, 45 (2008).

[46] Woodford JJ, Parlett CMA, Dacquin JP, Cibin G, Dent A, Montero J, Wilson K and Lee AF, *J. Chem. Technol. Biotechnol.*, 89, 73–80 (2014).

[47] Shu Q, Yang B, Yuan H, Qing S, Zhu G, *Catal. Commun.*, 8, 2159 (2007).

[48] Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA and Goodwin JG, *Ind. Eng. Chem. Res.*, 44, 5353–5363 (2005).

[49] Dacquin JP, Lee AF and Wilson K, Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals, *The Royal Society of Chemistry*, 416–434 (2010).

[50] Carrero A, Vicente G, Rodrıguez R, Linares M and Peso GL del, *Catal. Today*, 167, 148–153 (2011).

[51] Koh TS, Chung KH, *J. Kor. Ind. Eng. Chem.*, 19, 214 (2008).

[52] Kozhevnikov IV, *Chem. Rev.*, 98, 171–198 (1998).

[53] Ngamcharussrivichai C, Totarat P, Bunyakiat K, K, Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil," *Appl Catal A*, vol. 366, pp. 154-159 (2009).

[54] Cao F, Chen Y, Zhai F, Li J, Wang J, Wang X, Wang S, Zhu W, *Biotechnol. Bioeng.*, 101, 93 (2008).

[55] Lidstrom P, Tierney J, Wathey B, Westman J, Microwave assisted organic synthesis- a review, *Tetrahedron*, vol. 57, pp. 9225-9283, (2001).

[56] Patil PD, Gude VG, Mannarswamy A, Cooke P, Munson-McGee S, Nirmalakhandan N, Lammers P, Deng S, Optimization of microwave-assisted transesterification of dry algal biomass using response surface methodology, *Bioresource Technology*, vol. 102, no. 2, no. 1399-1405 (2011).

[57] Ma L, Chen WX, Zhao J, Zheng YF, Synthesis of Pr(OH)3 and Pr6O11 nanorods by microwave-assisted method: Effects of concentration of alkali and microwave heating time, *Journal of Crystal Growth*, vol. 303, pp. 590–596 (2007).

[58] Yan S, Kim M, Salley SO, Ng KYS, Oil transesterification over calcium oxides modified with lanthanum, *Appl Catal A Gen,* 360:163–70 (2009).

[59] Wang J, Chen Y, Wang X, Cao F, Aluminumdodecatungstophosphate (AL0. 9H0.3$PW_{12}O_{40}$) nanotube as a solid acid catalyst one-pot production of biodiesel from waste cooking oil, *BioResources*, 4:1477–86 (2009).

[60] Tanabe K, Yoshii N, Hattori H, Catalytic activity and selectivity of evacuated calcium oxide for isomerization of but-1-ene, *J. Chem. Soc D: Chem. Commun.*, Issue 9, p. 464 (1971).

[61] Liu X, He H, Wang Y, Zhu S, Piao X, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, *Fuel*, vol 87, pp. 216-221 (2008).

[62] Huaping Z, Zongbin W, Yuanxiong C, Ping Z, Shijie D, and Xiaohua L, Preparation of biodiesel catalyzed by solid super base of Calcium Oxide and its refining process, *Chin J.*

Catal., 27: 391-396 (2006).

[63] Serio Di, Ledda M, Cozzolino M, Minutillo G, Tesser R, and Santacesaria E, Transesterification of Soybean Oil to Biodiesel by using Heterogeneous Basic Catalysts, *Industrial and Engineering Chemistry Research,* 45: 3009-3014 (2006).

[64] Dossin TF, Reyniers MF, Berger RJ, and Marin GB, Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production, *Appl. Catal. B: Gen,* 67:136–148 (2006).

[65] Rubio Alba AC, Gonzalez Santamaria J, Josefa M, Heterogeneous transesterification processes by using CaO supported on Zinc Oxide as basic catalysts, *Catalysis Today*, 149: 281-287 (2010).

[66] Haas MJ, McAloon AJ, Yee WC, Foglia TA, A process model to estimate biodiesel production costs, *Bioresour Technol*, 97:671–678 (2006).

[67] Fjerbaek Lene, Christensen Knud V, Norddahl Birgir, A review of the current state of biodiesel production using enzymatic transesterification, *Biotechnology and Bioengineering*, Vol. 102, No. 5, (2009).

[68] Vulfson EN, In lipases – their structure, biochemistry & application, *Woolley P & Petersen SB, eds.,* 271-288, Cambridge univ. press, Cambridge (1994).

[69] Jegannathan KR, Abang S, Poncelet D, Chan ES and Ravindra P, Production of biodiesel using immobilized lipase-A critical review, *Crit. Rev. Biotechnol.*, 28: 253-264. DOI:10.1080/07388550802428392 (2008)

[70] Peilow AD and Misbah MMA, Immobilization of lipase enzymes and their application in the interesterification of oils and fats, *1st Edn., In: Methods in Biotechnology*, Vol.15: Enzymes in Nonaqueous Solvents: Methods and

Protocols. Vulfson EN, PJ Halling and HL Holland (Eds). Humana Press Inc., Totowa, New Jersey, ISBN: 089639293, pp: 627-649 (2001).

[71] Awang R, Ghazuli MR, and Basri M, Immobilization of lipase from Candida rugosa on palm-based polyurethane foam as a support material, *Am. J. Biochem. Biotechnol.*, 3: 163-166. ISSN: 1553-3468 (2007).

[72] Bhushan I, Parshad R, Gazi G and Gupta VK, Immobilization of lipase by entrapment in caalginate beads, *J. Bioact. Compatible Polym.*, 23: 552-562 (2008).

[73] Salah RB, Ghamghui H, Miled N, Mejdoub H and Gargouri Y, Production of butyl acetate ester by lipase from novel strain of Rhizopus oryzae, *J. Biosci. Bioeng.*, 103: 368-373 (2007).

[74] Nelson LA, Foglia A & Marman WN, *J Am Oil Chem Soc*, 73, 1191-1195 (1996).

[75] Hsiao MC, Lin CC, Chang YH, Microwave irradiation assisted transesterification of soybean oil to biodiesel catalyzed by nanopowder calcium oxide, *Fuel*, vol 90, Issues 5, pp.1963-1969 (2011).

[76] Oznur K, Tuter M & Aksoy HA, *Bioresour technol*, 83, 125-129 (2002).

Fabrication of Magnesium Based Metal Matrix Composites Through Friction Stir Processing – A Review

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Abstract
The scientists are concerned about the environment and they are inclined towards the light weight materials fabricated by green technology. Magnesium is one of the light weight materials which have low density, high strength to weight ratio, high damping capacity and excellent machinability. The properties of magnesium alloys ensure fuel economy, reduced harmful emissions which ultimately lead to healthy environment. Magnesium alloys exhibit appreciable decrease in mechanical properties when their components are subjected to high mechanical/thermal stresses that discourage their application for critical components in the automotive and aerospace sectors. So, to utilise the full capability of magnesium alloys, these alloys matrix are incorporated with reinforcement particles to produce Metal Matrix Composites (MMCs). The potential applications of the MMCs can be found in automotive, aerospace, biomedical and power industries. In order to produce MMCs keeping in mind the environmental effect, an eco friendly and a solid state technique named Friction Stir Processing (FSP) evolved which uses a non consumable rotating tool inserted into the workpiece for heating and softening the material. This results in material severe plastic deformation resulting in improved mechanical properties and refined grain structure. This paper presents the investigations of magnesium based metal matrix composite fabrication by FSP carried by researchers. It was concluded that MMCs are successfully fabricated through FSP and the processed region resulted in improved mechanical properties.

Keywords- *Metal Matrix Composites (MMCs); Friction Stir Processing (FSP); Magnesium Alloys; Reinforcement particles.*

Introduction

Magnesium alloys are replacing aluminium and steel in the aerospace and automobile industries and plastic in the electronic and computer industries due to light weight and excellent thermal and electrical conductivity. This increasing demand of magnesium alloys is due to its low density, high specific strength, good castability, weldability and machinability [1]. Magnesium alloys are developing their demand in industries mainly due to their high strength to weight ratio. However, most of magnesium alloys generally exhibit poor creep resistance at high temperatures, which discourages their industrial applications. Further, Mg alloys posses inferior formability at room temperature due to their Hexagonal Closed Packed (HCP) crystal structure; only three independent slip systems. Therefore, enhancement in ductility is the major concerns for the industrial application of magnesium alloys, this is the reason that Mg based MMCs came into existence. It is known that grain refinement is an effective approach to enrich the mechanical properties of magnesium alloys. Fine grained structures have been achieved by applying various techniques, e.g. grain refiners [2], altering, rapid solidification [3], spray co-deposition, recrystallization, and severe plastic deformation such as equal channel angular pressing (ECAP) [4]. Friction Stir Processing (FSP) is one of the severe plastic deformation (SPD) and solid state method which works on the principle of Friction Stir Welding (FSW) invented by The Welding Institute (TWI) in UK in 1991 [5]. The schematic illustration of FSP operation is shown in Figure 1.

FSP was initially applied for grain refinement of aluminum and magnesium alloys, but with the technology development it also becomes a useful process for fabricating Metal Matrix Composites (MMCs). Mishra et al. [6] fabricated the SiC/Al MMCs by FSP, and indicated that SiC particles were finely dispersed in the Al matrix, and good bonding with the Al matrix was generated. There are various conventional methods for fabricating MMCs such as powder metallurgy, laser melt treatment, plasma spraying, stir casting etc but these techniques results in deterioration of composite properties due to interfacial reaction between reinforcement particle and the metal matrix [7]. Moreover, These

techniques involve the material transformation from solid to liquid or vapour state during the process as compared to solid state technique. Further, precise control of processing parameters is required to obtain desired microstructure in surface layer after solidification. FSP is one of the solid state processing techniques which have proved its capability in fabrication of all variants of MMCs with little or no interfacial reaction with the reinforcement. The present paper aims at overall summary of the Friction Stir Processed (FSPed) MMCs for magnesium alloys and the influence of FSP parameters on the mechanical properties of produced composite.

2. Magnesıum Based Mmcs Fabrıcatıon By FSP

Metal Matrix Composite (MMCs) fabrication is one of the important applications of FSP. İt is defined as a multiphase material in which the surface of the material is changed by embodying secondary phase in the form of particles and fibres. Almost all literature reported groove filling and closing method for incorporation of secondary phase particles in the metal matrix. In this method, groove on the plate is closed with a pinless FSP tool to prevent escape of reinforcement particles, before performing the real FSP operation.

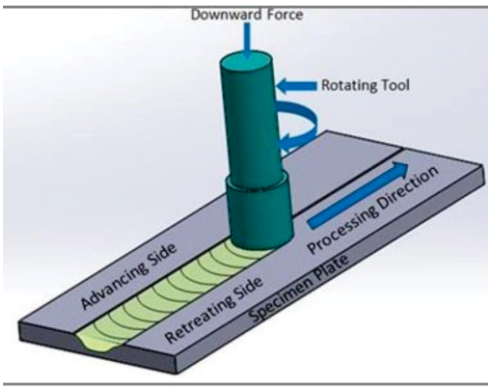

Figure 1 Schematic Illustration of FSP Technique.

Most of the FSP investigations is limited to AZ series magnesium alloy. Commonly used reinforcements for fabrication purpose are Titanium Carbide (TiC), Silicon Carbide (SiC), Aluminium Oxide (Al_2O_3), MWCNTs and Boron Carbide $(BC)_4$etc. This paper includes the different results regarding MMCs processsed by FSP with special emphasis on effect of different processing parameters. Morisada et al. [8] dispersed the Multi-walled carbon nanotubes (MWCNTs) in AZ31 matrix by FSP. After doing FSP, it was revealed that dispersion of MWCNTs particles in

AZ31 matrix depend on traverse speed of the rotating tool. Lower transverse speed exhibited fine distribution of reinforcement particles in the Mg alloy matrix since it gives enough time for heat flow to produce desired viscosity in the matrix. An excellent dispersion wass obtained for the sample FSPed at 25mm/min and 1500 rpm. Grain refinement due to FSP and extreme high strength of MWCNTs leads to increase of microhardness in composites. Maximum microhardness obtained is 78 Hv compared to 55 and 41 Hv of FSPed without reinforcement and as cast alloy respectively. Also, pinning effect exhibited by MWCNTs increase mechanical properties due to reduction in grain growth of AZ31 matrix. Morisada et al. [9] further developed SiC/AZ31 MMCs by FSP. SiCp results in grain refinement after FSP through recrystallisation process. Due to grain refinement by SiC particles and high hardness of particles, microhardness of stir zone with SiC particles is high compared to parent Mg alloy and FSPed Mg alloy. Fine grain structure of AZ31 obtained by FSP becomes unstable at high temperature while that of AZ31 having SiC particles is not affected by heat treatment process.

Number of FSP passes also affects the grain distribution during FSP. C.J. Lee et al. [10] fabricated AZ61/SiO_2 nanocomposite by FSP. After FSP, the nano-SiO_2 particles were observed to be clustered in a size ranging from 0.1 to 3μm and the level of clustering was found to be reduced for the composites produced with higher number of passes and nano-particles were uniformly dispersed after four FSP passes. Moreover, M. Dadashpour et al. [11] fabricated AZ91/SiO_2 by FSP and concluded that reinforcement particles were distributed evenly inside the base metal matrix without any defect formation. Also, agglomeration of nanoparticles is observed at lower number of FSP passes, which can be corrected by increasing the no. of FSP passes. This leads to increase of strength of material. Further, Navazania and Dehghani [12] fabricated AZ31/ZrO_2 nanopowders by FSP and found that increase in the passes of the FSP led to finer grains as well as less agglomeration of the ZrO_2 particles, thus enhancing the pinning effect of particles. This pinning effect will retard the grain growth which leads to improvement of mechanical

properties such as strength and hardness. Navazania and Dehghani [13] further synthesized 5μm TiC particles on the surface of AZ31 magnesium alloy matrix and observed that by incorporating TiC particles; average grain size was reduced from 40 μ to 12 μ. Also, TiC particles had pinning effect on Grain Boundaries which restrict grain boundary movement and therefore grain growth is retarded. Intense temperature and severe plastic deformation results in fine microstructure. Also, discontinuous dynamic recrystallization is the main mechanism responsibel for refinement of microstructure. Average hardness is increased from 50Hv to 79Hv after embodying reinforcement particle. Recently, M. Balakrishnan et al. [14] fabricated TiC/AZ31 MMCs using FSP. There is even distribution of TiC particles without any formation of clusters. Moreover, there is no interfacial reaction between the Mg matrix and TiC particles due to inadequate temperature developed in the matrix which can start the reaction. Jiang et al. [15] successfully synthesized nano-SiO_2 particles in the AZ31 Mg a matrix through FSP. The authors revealed that SiO particles resulted in grain refinement of equiaxed ultrafine grains with sizes of less than 1 μm. Moreover, hardness of the SiO/AZ31 composites was found to be 90 Hv which was nearly two times than that of the original alloy. This increase in hardness was attributed to dispersion of high strength SiO particles and grain refinement taking place in the stir region of AZ31/SiO composites. Asadi et al. [16] fabricated AZ91/SiC surface nanocomposite layer by 8 FSP passes with the help of groove filling and closing method. From a starting grain size of 150 μm, grain refinement was achieved up to 600 nm and 7.21 μm in AZ91/SiC composite and FSPed AZ91 without SiC particles, respectively. It was observed that the increase in the tool rpm influenced the microstructure evolution due to the generation of higher amounts of heat, which led to grain growth and also decreased the surface hardness. But increase in the tool traverse speed resulted in lower grain size and higher hardness. Microhardness increased from 63 Hv to 115 Hv and 90 Hv for the composite and AZ91 without SiC particles, respectively, after eight FSP passes. A higher level of uniformity in

the distribution of SiC was achieved by changing the tool rotating direction. In a similar work by Khayyamin et al. [17], FSP was done to fabricate AZ91/SiO_2 surface composites at three different traverse speeds (20, 40, 63 mm/min) and a fixed rpm of 1250. It was revealed that with increase in tool travel speed, grain size reduced which ultimately increased the hardness. Therefore, it is evident from the following discussion that higher tool travel speeds decrease the localized heat and reduce the grain growth issue during FSP.

Some of the studies also mentioned about the optimum traverse speed which will produce the sound and defect free processed zone. Similar to the work of Asadi et al. [16], Erfan and Kashani-Bozorg [18] observed the influence of tool rpm and tool traverse speed on the distribution of nano-sized SiC particles in AZ31 magnesium alloy. It was reported that as tool rpm increases, the level of clustering of SiC particles was found to be reduced. Also, the grain size was reduced with the increase in tool traverse speed due to the less generation of heat. Another important observation from the work is the development of tunneling defect with higher traverse speeds. Therefore, it is clear from the above studies that there should be an optimum traverse speed which can achieve grain size reduction along with the sound and defect free stir zone.

Most of the above mentioned literature review is concerned with grain refinement, microhardness improvement, pinning effect of particles. Some of the research is also done on the improvement of mechanical properties such as UTS and elongation. K. Sun et al. [19] synthesized high strength AZ63/SiCp nano-composite using FSP. In their study, 5 FSP passes is done to fabricate the 40nm SiC particles on AZ63 magnesium alloy. Moreover, SiC particles were ultrasonically dispersed in ethanol before filling into groove to avoid clustering of nanoparticles. Some of the conclusions were: Base metal containing irregular coarse second phase intermetallic compound $Al_{12}Mg_{17}$ get dissolute after 5 pass FSP. Only two phases occurred in the in SiC-AZ63 composite which clearly states that no interfacial reaction occurred between the base material and reinforced particles during FSP. Vicker hardness was found to be increased from 80 Hv to 109 Hv. Further, UTS was

found increased from 160 Mpa to 312 MPa. The strengthening mechanism of composites was explained by the pinning effect of particles at grain boundaries and the particles present inside the grain which prevent the dislocation slipping as shown in fig.4. This was explained like, as the tensile stress is increasing, the dislocation inside the grain began to slip. The existence of nanoparticles can stop the dislocation slipping. The dislocation line would form a dislocation loop around the nanoparticles, which increase the dislocation density, so the material would need more stress to deform.

FSP parameters like traverse speed, pin profile, rotational speed, tool tilt angle and Penetration Depth play role in the modification of microstructure and defect formation. Parviz Asadi et al. [20] fabricated 5μm SiC/AZ91 surface composite by FSP and studied the effect of process parameter, Penetration Depth (PD). There is an optimum penetration depth which results in formation of defect free FSPed specimen. At high PD, sliding mode of friction changes to sticking mode of friction which results in sticking of base metal to the tool. But at low PD, a longitudinal crack develops in the processing zone which results in tunneling type of defects in the stirred zone. Optimum PD depends on tool tilt angle and rotational speed like, increasing rotational speed and decreasing tilt result in decrease of PD. Also, there is an opposite effect of traverse speed and rotational speed on grain growth. Increase of traverse speed leads to decrease in grain size while increase of rotational speed leads to an increase in grain size. Therefore, by adding SiC particles, grain structure is refined from 150 to 7.17 μm and microhardness is increased from 63 to 96 Hv.

M. Azizieh et al [21] investigated the effect of rotational speed, pin profile, no. of FSP passes and particle size on the AZ31/Al_2O_3 nano-composite synthesized by FSP. Firstly, the authors concluded that the threaded probe tool is best among the non threaded probe tool and three flute probe tool, since threaded profile fabricate the composites without any development of cavity and with good particle distribution unlike the tunnelling defect and tool jamming exhibited by three flute profile while poor particle dispersion exhibited by non threaded probe. All further investigations were

done on threaded profile produced MMCs. Secondly, the authors investigated the combined effect of rotational speed and no. of FSP passes on the particle dispersion, grain size and microhardness of the composite fabricated by threaded probe tool. It was revealed that with increase in rotational speed from 800 to 1200, the average grain size of the composite was increased due to greater heat input while with increase in no. of passes from 2 to 4; average grain size was reduced at a fixed rpm. Moreover, with increase in rpm and no. of passes, the agglomeration of nanoparticles reduces i.e. good particle distribution due to higher heat input and more material flow in the processed zone. One of major finding from this study was that at higher rotational speed of 1200, even the finely distributed Al_2O_3 particles were not able to retard the grain growth in the stir zone due to the combined effect of shattering or fragmentation of matrix grains and alumina particles, and grain growth by heat generation. Due to these effects, composites fabricated at higher rpm of 1200 shows less microhardness value (86 Hv at 4 passes) compared to the composites (92 Hv at 4 passes) processed at lower rpm of 800. At last, authors studied the effect of particles size ranging from no particle addition to micro particle (0.35 μm and 1 μm) and ultimately to nanoparticles (35 nm) on grain size and microhardness of the composite. Results shows that grain size was effectively refined in case of nanocomposite compared to composite with micro-particles, FSPed sample without particles addition and initial state of matrix. Also, with decrease in particle size the hardness value increases i.e. the nanocomposite had the highest hardness value of 90Hv in the stir zone compared to other studied particles. This is due to higher distribution of nanoparticles which ultimately lead to severe pinning effect at the grain boundary of the matrix.

Some studies also include the rotational speed and traverse speed ratio (ω/ν) as a FSP parameter. Faraji and Asadi [22] synthesized AZ91 with Al_2O_3nanoparticles (30 nm) through FSP and investigated the effect of rotational speed/traverse speed ratio (ω/ν), FSP tool pin profile and no. of FSP passes on the microstructure and microhardness of the developed nanocomposite. Initially, with the help of square and circular profile FSP tool, investigaters fabricated the

composite at a rotational speed of 900 rpm and traverse speed of 40 mm/min and revealed that it was difficult to achieve uniform dispersion of particles even in low traverse speed in the case of circular probe tool. This is due to the absence of pulsating stirring action in case of circular probe tool as this action magnified the mixing of particles in the matrix. All further investigations were carried out using square probe tool. It was revealed that higher ω/ν ratio results in good distribution of Al_2O_3 nanoparticles i.e. less clustering of alumina particles and consequently smaller grain size of the composite layer. Thus, optimum conditions for developing the sound surface layer was achieved by square tool and rotational speed of 900 rpm and traverse speed of 40 mm/min. Moreover, microhardness was also accelerated at higher ω/ν ratio due to the small grain size which was justified by Hall-Petch relationship. It was also reported that increase in number of passes results in increase of microhardness; since more passes homogenizes the particles dispersion, decreases the alumina clustering and consequently decreases the grain size.

Conclusion

The FSP technique is an effective method to fabricate metal matrix composites. The findings are as below:

- Mostly AZ series based Mg alloys surface composite are developed with the help of FSP. Important machine parameters considered during FSP which have considerable effect were tool traverse speed, rotational speed, and penetration depth.
- It was observed that in the fabrication of MMCs, tool traverse speed and rotational speed have both positive and negative effects. Increase in tool rotational speed results in increase of grain size which decreased the microhardness due to the more heat input but higher rotational speed results in homogeneous distribution and breaking up of clusters. Moreover, greater rotational speed accelerates the pinning effect of particles at the grain boundary which deaccelerates the grain growth and thus increasing strength and hardness. But another investigation revealed that even the finely distributed AlQ particles were

not able to retard the grain growth due to the combined effect of shattering of matrix grains and alumina particles, and grain growth by heat input. While increase in traverse speed exhibited decrease in grain size and grain refinement which results in increase of hardness due to less local heat input.

Ÿ Number of FSP passes also affect the fabrication of MMCs by reducing the clustering of particles. Multi-pass FSP results in reduction of size of cluster and uniform distribution of reinforcement particles and thus decreases the grain size of matrix.

References

[1] B.L. Mordike and T. Ebert, *Magnesium Properties — applications — potential*, Materials Science and Engineering A302 (2001) 37–45.

[2] Ma Qian and A. Das, *Grain refinement of magnesium alloys by zirconium: Formation of equiaxed grains,* Scripta Materialia 54 (2006) 881-886.

[3] J. Cai, G.C. Ma, Z. Liu, H.F. Zhang, Z.Q. Hu, *Influence of rapid solidification on the microstructure of AZ91HP alloy,* Journal of Alloys and Compounds 422 (2006) 92–96.

[4] K. Mathis, J. Gubicza, N.H. Nam, *Microstructure and mechanical behavior of AZ91 Mg alloy processed by equal channel angular pressing,* Journal of Alloys and Compounds 394 (2005) 194-199.

[5] R.S. Mishra and Z.Y. Ma, *Friction Stir Welding and Processing,* Materials Science and Engineering R 50 (2005) 1 – 78.

[6] R.S. Mishra, Z.Y. Ma, I. Charit, *Friction stir processing: a novel technique for fabrication of surface composite,* Materials Science and Engineering A341 (2003) 307–310.

[7] Vipin Sharma, Ujjwal Prakash, B.V. Manoj Kumar, *Surface composites by friction stir processing: A review,* Journal of Materials Processing Technology 224 (2015) 117–134.

[8] Y. Morisada, H. Fujii, T. Nagaoka, M. Fukusumi, *MWCNTs/AZ31 surface composites fabricated by friction stir processing,* Materials Science and Engineering A 419 (2006) 344–348

[9] Y. Morisada, H. Fujii, T. Nagaoka,

M. Fukusumi, *Effect of friction stir processing with SiC particles on microstructure and hardness of AZ31 Y,* Materials Science and Engineering A 433 (2006) 50–54.

[10]C.J. Lee, J.C. Huang, P.J. Hsieh, *Mg based nano-composites fabricated by friction stir processing,* Scripta Materialia 54 (2006) 1415–1420.

[11]M. Dadashpour, A.Mostafapour, R.Yesildal, S.Rouhi, *Effect of process parameter on mechanical properties and fracture behavior of AZ91C/SiO $_2$ composite fabricated by FSP,* Materials Science & Engineering A655 (2016) 379–387.

[12]Mohammad Navazania and Kamran Dehghani, *Fabrication of Mg-ZrO$_2$surface layer composites by friction stir processing,* Journal of Materials Processing Technology 229 (2016) 439–449.

[13]Mohammad Navazania and Kamran Dehghani, *Investigation of microstructure and hardness of Mg/TiC Surface Composite Fabricated by Friction Stir Processing (FSP),* Procedia Materials Science 11 (2015) 509-514.

[14]M. Balakrishnan, I. Dinaharan, R. Palanivel, R. Sivaprakasam, *Synthesize of AZ31/TiC magnesium matrix composites using friction stir processing,* Journal of Magnesium and Alloys 3 (2015) 76-78.

[15]Yupei Jiang, XuyueYang, Hiromi Miura, Taku Sakai, *Nano-SiO_2 particles reinforced Mg Alloy Produced FSP,* Reviews on Advanced Materials Science 33 (2013) 29-32.

[16]P. Asadi, M.K. Besharati Givi, G. Faraji, *Producing Ultrafine-Grained AZ91 from As-Cast AZ91 by FSP,* Mater. Manuf. Process. 25 (2010) 1219–1226.

[17]D. Khayyamin, A. Mostafapour, R. Keshmiri, *The effect of process parameters on microstructural characteristics of AZ91/SiO $_2$ composite fabricated by FSP*, Materials Science & Engineering A559 (2013) 217–221.

[18]Y. Erfan and S.F. Kashani-Bozorg, *Fabrication of Mg/SiC nanocomposite surface composite layer using FSP technique,* International Journal of Nano science 10 (2011) 1073.

[19]K. Sun, Q.Y. Shi, Y.J. Sun, G.Q. Chen, *Microstructure and*

mechanical property of nano-SiCp reinforced high strength Mg bulk composites produced by friction stir processing, Materials Science and Engineering A 547 (2012) 32–37.

[20]Parviz Asadi, Ghader Faraji, Mohammad K. Besharati, *Producing of AZ91/SiC composite by friction stir processing (FSP),* International Journal of Advanced Manufacturing Technology 51 (2010) 247–260.

[21]M. Azizieh, A.H. Kokabi, P. Abachi, *Effect of rotational speed and probe profile on microstructure and hardness of AZ31/Al$_2$O$_3$ nano composites fabricated by friction stir processing,* Materials and Design 32 (2011) 2034–2041.

[22]Ghader Faraji and Parviz Asadi, *Characterization of AZ91/alumina nanocomposite produced by FSP,* Materials Science and Engineering A528 (2011) 2431–2440.

Performance Analysis of Biogas Run Dual- Fueled Diesel Engine

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Abstract

In this work a systematic experimental investigation is carried out for the performance of the biogas run compression ignition diesel engine in dual fuel mode. Many Experiments were conducted in a modified engine test unit to run biogas under dual fuel operations. For an equal power output from each of the diesel and dual fuel engine operation, the performance results were evaluated. This type of comparison approach can decide the feasibility of a dual fuel engine usage in place of a conventional diesel engine.

Keywords: *Biogas, dual fuel engine*

Introduction

One of the most serious problems that the world is being confronted is the use of limited fossil fuel like petrol, diesel etc. which has severely harm the environment. So these days' alternatives to this fossil fuel so-called renewable source of energy has been a topic of investigation for researchers. Among the many

different available energy sources Biogas from anaerobic digestion of animal manure waste can be used and has proved to meet the demand of environment concern [1]. Biogas may be characterized based on its chemical composition and physical characteristics, which result from it. It is primarily mixture of methane (CH_4) and inert carbonic gas (CO_2). However, the name "biogas" gathers large variety of gasses resulting from specific treatment processes, starting from different organic wastes like industries, animal or domestic origin waste etc. Earlier Biogas was used for cooking in the rural household but it can be also used for generating shaft power and electricity. Biogas has variety of combustion and compositional characteristics compared to natural gas, so it needs a different system of preconditions compared to the combustion of natural gas [2]. One way of using this biogas can be duel fueled compression ignition diesel engine. The basic concept behind this type of engine is the use of primary fuel also known as gaseous fuel and pilot fuel. The duel fuel engines are classified into two categories depending on the utilization of pilot and gaseous fuel.one category includes the injection of small amounts of liquid fuel to provide ignition to a lean mixture of gas and air. Here the bulk of energy comes from the gaseous fuel (also called primary fuel). And another one is associated with the addition of some gaseous fuel to air in a fully operational diesel engine. The interest of this paper lies within the second category of the dual fueled engine. Earlier there was obscurity about the feasibility of the engine to be run by biogas but the compression of biogas is possible and the application of biogas as a fuel for dual fuel diesel-biogas engines is feasible and economical (Cheng-qiu et al.,1989). An investigation on small biogas/diesel dual-fuel engine for on-farm electricity generation and it was found that the, dueled fuel operation in diesel engine showed superior efficiency compared to normal diesel operation (N. Tippayawong et al.,2007).The gas engine tests for the energy utilization was concluded for the development of experimental variants useful for improvement of

biogas produced from pig manure and plant additives and establish the satisfied condition for running the heat engine properly (Attila Meggyes et al.,2012). It was found that found that a small addition of O to intake combustion air improve combustion stability in a biogas-diesel engine. The additional O_2 helps to attenuate negative effects of CO_2 in combustion such as decreases in overall gas-air mixture temperature and low burning velocities of biogas regarding methane (Cacua et al.,2009).

Considering the above literature review it is found that the researchers have done marvelous development in the context of combustion characteristics, improvement of energy utilization, quality improvement of biogas and designing of engine parameter for power output. The present study deals with the study of the performance of dual fuel compression ignition diesel engine which is run by biogas. Here the biogas will be added to the air in a fully operational diesel engine. Initially, baseline performance tests are carried out with the engine operating on diesel fuel only and then with biogas. The main objective is to compare the performance of dual fuel compression ignition diesel engine with a normal diesel engine in terms of brake power, brake power efficiency, volumetric efficiency, exhaust temperature and air consumption.

2. Experimental

2.1 Biogas and pilot Fuel

Biogas which has been employed as the gaseous fuel mixed with the air for the dual fuel operation. biogas was collected from the Gobar gas plant, Yupia, Naharlagun, Arunachal Pradesh, India. It was produced by the anaerobic digestion of cow manure. In our investigation, the standard diesel is used as the pilot fuel for the experimental work for both baseline and dual fuel mode. This diesel is supplied through the injection pump from the fuel tank under the gravity fed.

2.2 Engine test rig set-up and procedure

The engine used for the investigation is the Petter AA1 Diesel Engine. It is a single cylinder constant-speed, four-

stroke, direct injection, water-cooled diesel engine. The rated power is 2.6kW at 3600 min^{-1} and it has a bore of 70mm and stroke of 57mm. It is designed conventional fuel injection system and loaded with a hydraulic dynamometer. The injection nozzle has three holes of 0.3mm diameter with a spray angle of 120°. The liquid fuels are supplied to the engine injection pump from a fuel tank under gravity feed. Type K thermocouples are installed on different locations of engine setup and connected to a data logger for measuring various temperatures. The airflow to the engine was monitored by passing the intake air through an air box with orifice meter and manometer. The pressure drop was measured by an inclined tube manometer, calibrated in millimeters of diluted ethyl alcohol. The air flow was calculated from the viscous Flowmeter calibration. During the dual fuel operation, Biogas was supplied through a plastic pipe and mixed with inlet air in simple mixing chamber consists of a T-junction of a tube or flow channel(fig.1) with an inlet for air and for gasses each and an outlet for the mixture of both. The outlet is connected to the intake channel or manifold of the engine. the flow rate of Biogas was measured in the Biogas Flowmeter. figure.2 shows the schematic view of dual fuel engine and the connection between various components.

Table 1. Characteristics of Diesel, Biogas, Manometry fluid and Air used

	Low heat value	Density
Biogas	5000 kcalm-3	-
Diesel	44.80 MJ kg-1	820 kg m-3
Diluted ethyl alcohol	-	789 kg/m^3
Air	-	1.225 kg/m3 at NTP

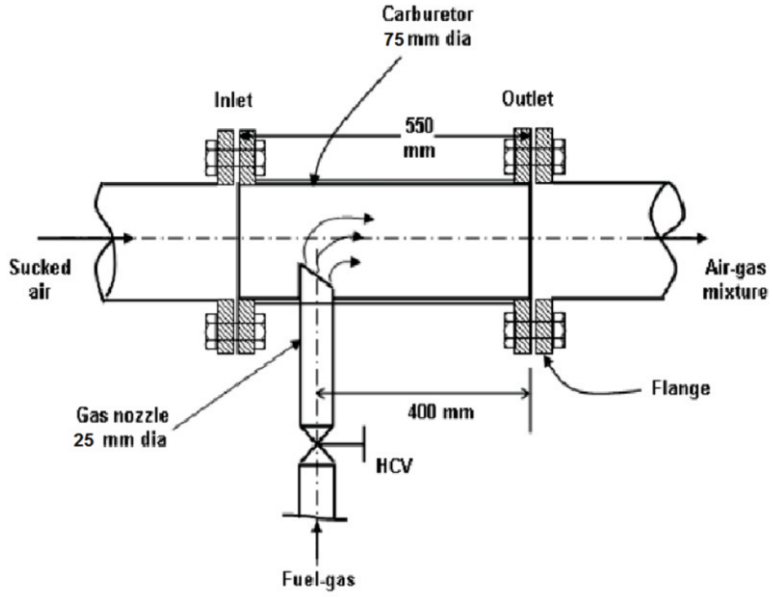

Fig 1. - T-joint tube type mixer

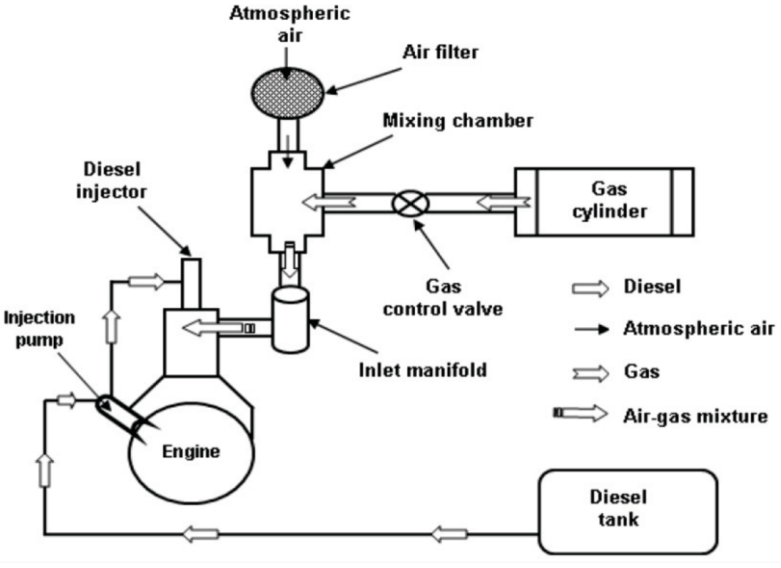

Fig2. - Schematic Diagram of Dual Fuel Diesel Engine

Initially, the engine was run idly at 1500 rpm without any load to reach stable operating conditions for 20 minutes. To establish a basis for comparison of results baseline performance tests was carried out with the engine operating on diesel fuel only. The load was varied in steps from 1.5N to 4N in the hydraulic dynamometer. For each load all the required parameters like rpm, exhaust temperature, the difference in the liquid level of the manometer, Volume of diesel fuel consumption by the engine in one minute etc. are noted. For the biogas dual fuel mode operation, biogas flow was opened up slowly from the gas balloon and allowed biogas to reach the gas carburetor. The homogeneous air-gas mixture from carburetor was hence sucked into the cylinder to take part in the dual fuel combustion via engine manifold. During the process, engine speed was increased due to addition extra chemical energy from biogas. To maintain a constant speed for both diesel and dual fuel modes, the quantity of diesel was varied by adjusting the liquid fuel cut-off valve. The data acquisition was undertaken similar to baseline tests for each step load.

To present the air consumption measured in kghr $^{-1}$ and volumetric efficiency the following expression is adopted

Air flow rate, $F = C_d \times \frac{\pi}{4} \times d^2 \times \sqrt{\frac{2gh \times W_{den}}{A_{den}}} \times 3600 \times A_{den}$

where C_d is discharged coefficient, d is the diameter of orifice meter in millimeter, h is the height of manometry fluid (diluted ethyl alcohol) in millimeter,

Volumetric efficiency,

$$\eta_V = \frac{F}{(\pi/4) \times D^2 \times L \times \frac{N}{n} \times 60 \times K \times A_{den}} \times 100$$

Where D is the diameter of cylinder in millimeter, L is the stroke length of cylinder in millimeter, N is the speed in revolution per minute, K is the number of cylinder andn=1(for Two stroke engine), =2(for four stroke engine)

The brake power and brake thermal efficiency are calculated according to

Brake Power, BP $\frac{2x3.142xNxWxR}{60x1000}$

Where, X is the cc liquid fuel consumption of engine in cc/min) and ρ_{Lf} is the liquid fuel density in kg.m^{-3}

Thermal brake efficiency $= \frac{BP \times 3600}{\dot{m}_d \times LHV_d} \times 100$

for normal diesel operation,

$$= \frac{BP}{\dot{m}_d \times LHV_d + \dot{m}_g \times LHV_g} \times 100$$

for dual fuel operationWhere, LHV_d Low heating value of diesel and LHV_g is Low heating value of biogas in $MJ.kg^{-1}$ All these performance parameters were obtained from the above relation and compared the performance of the dual fuel compression ignition diesel engine and normal compression diesel engine. During the process, the serious attention was given for the proper functioning of each component during the experiments.

3. Results And Discussion

The results of the experiments conducted for the comparison of dual fuel compression ignition diesel engine with normal compression diesel engine are shown in figs 3,4,5 and 6. The patterns of variation for each parameter are found to be almost same. Fig.3 shows the greater air consumption for diesel mode than dual mode at equal loading conditions. more substitution of air takes place by fuel at higher load. Fig.4 shows lower volumetric efficiencies for dual fuel operations than diesel mode. The higher temperature of the retained exhaust gas preheats the incoming fresh air and lowers the volumetric efficiency and at higher power outputs higher biogas substitution displaces a greater proportion of air. The brake power and the brake thermal efficiency obtained for diesel were more than that for dual fuel mode as shown in figure 5 and 6. A considerable reduction in thermal efficiency (about 19% to 40%) was observed under dual fuel modes as compared to diesel mode for the entire load range. This is mainly due to the lower heating value of biogas and by increasing the quality of biogas giving the higher heating value may increase the efficiency to greater extend. Lastly, fig.7 shows the Variation of Exhaust

Load	A/F	VEF %	BRAKE POWER Kw	BTE %	EXHAUST TEMP.(0C)
0.5	5.60	0.69	0.06	0.58	162
1.5	6.00	0.69	0.17	1.69	163
2	4.10	0.69	0.22	1.78	165
2.5	3.59	0.68	0.28	2.01	166
3	2.94	0.67	0.33	2.06	167
3.5	3.23	0.66	0.389	2.68	168
4	2.92	0.66	0.41	2.82	169

Table 2. Experimental observations and performance parameters for diesel

LOAD	A/F	VEF %	BRAKE POWER kW	BTE %	EXHAUST EMP.(^{0}C)
1.5	33.19	85.94	0.30	10.68	197
2	25.78	82.97	0.38	12.03	198
2.5	24.33	81.63	0.32	9.89	200
3	21.20	80.14	0.35	10.24	201
3.5	17.66	80.59	0.41	10.91	202
4	16.03	79.36	0.50	12.30	202

Table 3. Experimental observations and performance parameters for dual

Temperature in which the temperature for dual mode was less than diesel mode.

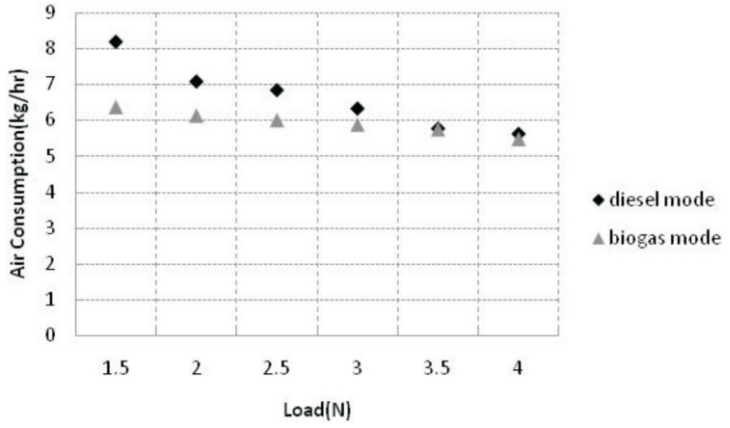

Fig3. Variation of air consumption rate with load from diesel and duel fuel operation

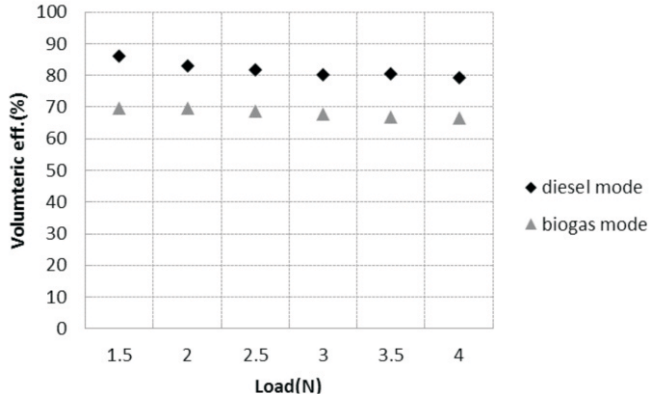

Fig 4. Variation of volumetric efficiency with load from diesel and duel fuel operation

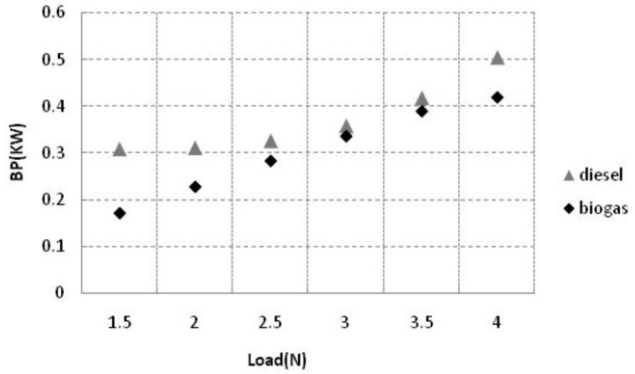

Fig5. Variation of brake power with load from diesel and duel fuel operation

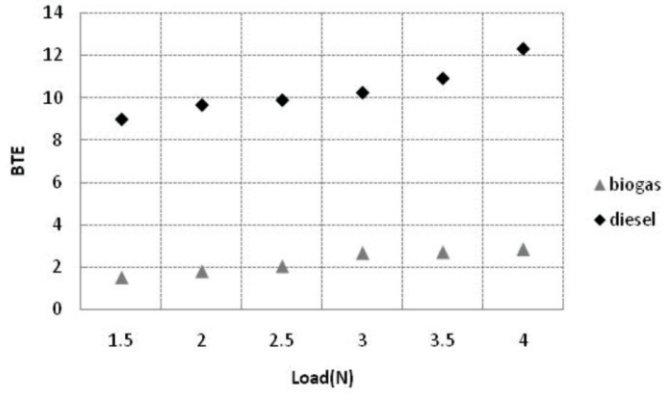

Fig6. Variation of brake thermal efficiency with load from diesel and duel fuel operation

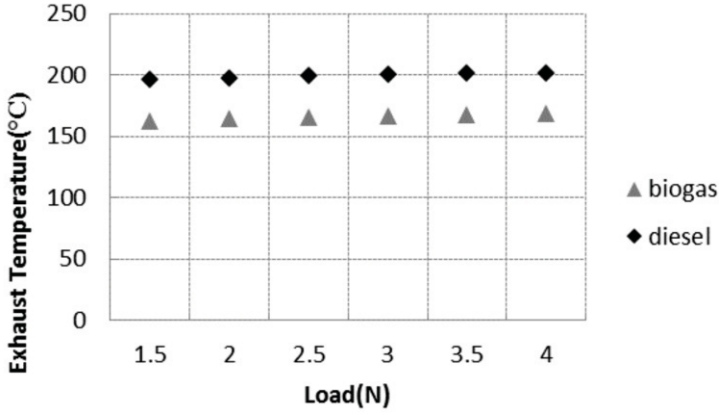

Fig7.Variation of exhaust temperature with load from diesel and duel fuel operation

Conclusion

Diesel engines are established as a unique combination of energy efficiency, power, reliability, and durability. They play a vital role in transport sectors, farm and construction purpose, power generation, etc. But these engines adopt fossil diesel fuel-based technology which contributes to the production of greenhouse gasses by CO and CO_2 emissions. In order to reduce these carbon emissions, there are possible and available clean diesel technologies viz., alternative fuels, hybrid-electric power and fuel cell etc. Use of clean gaseous fuel like biogas, alternative to diesel, is one of the techniques which have the potential for reducing greenhouse gas emissions. dual fuel compression ignition diesel engine can be used for obtaining power from biogas. In the present work, an experimental investigation has been carried out to evaluate the various performance parameters of dual fuel compression ignition diesel engine compared it with the normal diesel engine. There was an increase in brake power and brake thermal efficiency with a load for both diesel and dual fuel mode. The brake power for diesel mode was greater than dual fuel mode. The maximum brake power obtained for diesel mode was 0.50kW at 4N load, for dual fuel mode was 0.41kW at 4N load. thermal efficiency obtained for diesel mode was 12% at 4N load and for dual mode was 2.82% at 4N load. Use of biogas having higher heating valve can increase the brake power and the brake thermal efficiency of the dual fuel engine. This indicates the adoption of this biogas may reduce the diesel fuel cost which causes higher CO and CO2 emissions. Although the power obtained through the dual fuel compression ignition diesel engine was found to be less in the experiment conducted but this dual-fuel engine appeared to perform well and have great potential for producing power and also meet the criteria of environment concern.

References

[1] Tippayawong N., Promwungkwa A. and Rerkkriangkrai P. (2007), "Long-term operation of a small biogas/diesel dual-fuel engine for on-farm electricity generation". Biosystems Engineering, Vol. 98, No. 1, pp. 26–32

[2] Bari S. 1996, “Effect of carbon dioxide on the performance of biogas/diesel dual-fuel Engine”. Renewable Energy, Vol. 9, No. (1–4), pp. 1007–1010

[3] Seung H.Y., Chang S.L., 2011, “Experimental investigation on the combustion and exhaust emission characteristics of biogas–biodiesel dual-fuel combustion in a CI engine”. Original Research Article: Fuel Processing Technology, Vol. 92, pp. 992-1000

[4] Attila M. and Valéria N. (2012), “Biogas and Energy Production by Utilization of Different Agricultural Wastes”. Vol. 9, No. 6

[5] Sahoo B.B., Sahoo N. and Saha U.K.(2009), “Effect of engine parameters and type of gaseous fuel on the performance of dual-fuel gas diesel engines–A critical review"”. Renewable and Sustainable Energy Reviews, Vol. 13, pp. 1151–1184

[6] AbdAlla G.H., Soliman H.A., Badr O.A. and AbdRabbo M.F.(2000), “Effect of pilot fuel quantity on the performance of a dual fuel engine”. Energy Conversion and Management, Vol. 41, No. 6, pp. 559–572

[7] Jiang, C., J, Liu, T., and Zhong, J. 1989, “A study on compressed biogas and its application to the compression ignition dual-fuel engine”. Biomass, Vol. 20, pp. 53–59

[8] Sahoo BB. Clean development mechanism potential of compression ignition diesel engines using gaseous fuels in dual fuel mode. Ph.D. thesis. India: Centre for Energy, IIT Guwahati; 2011.

[9] Yoon SH, Lee CS. “Experimental investigation on the combustion and exhaust emission characteristics of biogas – biodiesel dual-fuel combustion in a CI Engine”. Fuel Process Technol 2011;92(5):992–1000.

[10] Henham A, Makkar M. “Combustion of simulated biogas in a dual-fuel diesel Engine”.Energy Convers Manage 1998;39(16–18):2001–9.

Performance Evaluation of Fouled Evaporator Vapour Compression System

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Abstract

In this paper, effect of evaporator fouling is measured on the performance of a vapour compression system with refrigerants HFO1234yf as a substitute to HFC134a. The condenser coolant temperature ($T_{in,\ cond}$) has been varied between 35 - 40°C to evaluate the effect of fouling, while keeping the evaporator air inlet temperature ($T_{in,\ evap}$) and efficiency of compressor (ηcp,isn) constant. The conductance of evaporator has been reduced up to 50% for analyzing the effect of fouling on the system performance. A simulation program is developed in Engineering Equation Solver (EES) for computing the results. The fouling decreases the compressor power, cooling capacity and COP. The second law efficiency is also observed to decrease with decrease in the evaporator conductance.

Key Words *Vapour Compression; Compressor; Evaporator; Fouling; R1234yf; R134a*

Introduction

Refrigeration involves heat transfer from a low-temperature region to a high-temperature region. This process is typically utilized by means of a Vapour compression refrigeration cycle (VCRC) involving a particular refrigerant. In recent past the most commonly used refrigerants are R11, R12, R500, R22 and R123, but due to

their high ODP these refrigerants have either been phased out or are to be phased out in near future. In recent years, HFC134a is used in many refrigeration applications viz. automobile air-conditioning, refrigerators. HFC134a has high GWP, and hence needs replacement by a low GWP refrigerant.

Calm [1] reported HFO1234yf is a low GWP refrigerant. Ding [2] and Cabello et al. [3] have modeled the system components and computed the performance of the vapour compression system. Lee and Jung [4] worked on mobile air-conditioning bench tester under summer and winter conditioning for HFO1234yf and HFC134a. And their results showed that the COP, cooling capacity and discharge temperature (Compressor) for HFO1234yf are 2.7%, 4.0%, and 6.5℃ lower as compared to HFC134a. Jarall [5] compared the performance of HFO1234yf with HFC134a at nominal output power (550W) in a refrigeration plant. Their results showed that HFO1234yf gives less cooling capacity, COP, and compressor efficiency by 3.4-13.7%, 0.35-11.88% and 0-6.3% in comparison to HFC134a. Reasor et al. [6] studied that due to environmental concerns, refrigerants with a low global warming impact are gaining importance in the refrigeration industry. Refrigerant R1234yf has a low GWP of 4, compared to 1430 for R134a, and has thermodynamic properties similar to R134a, making it a desirable choice for future automotive refrigerants.

The literature survey shows that HFOs are next generation refrigerants. These are the alternative refrigerants but their performance evaluation is must, before putting them into commercial use. Their performance should be evaluated under ideal and actual working conditions.

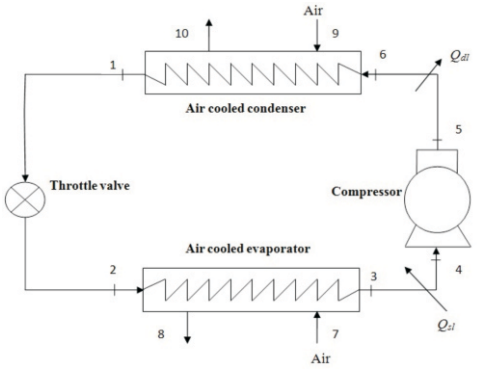
During the operation of system, the performance under actual working condition is dependent on the fouling of heat exchanger. The scale deposition on the surfaces of heat exchanger (evaporator) tubes increases thermal resistance and hence affecting the system performance. The sensitivity of the heat exchanger to fouling is strongly dependent on the type of fouling as well as the specifics of the heat exchanger geometry. Ahn et al. [7] examined experimentally the air-side

particulate fouling in fin-and-tube heat exchangers of air conditioners. They observed that the important parameters influencing the fouling of heat exchangers are the concentration and size of indoor pollutants, the filter efficiency, hydrophilicity of fin surfaces and fin spacing. The pressure drop of heat exchangers increases due to the deposition of indoor pollutants larger than 1 μm in size and increases up to 44% in the samples used for 7 years. The air-side particulate fouling degrades the cooling capacity by 10-15% in the samples. Yang et al. [8] discussed the impact of evaporator fouling on the performance of R22 packaged air conditioners. In this study it was found that the equipment cooling capacity is reduced with fouling primarily because of a decrease in airflow due to the increased pressure drop. Fouling affects evaporator-side fan power which in turn affects the equipment EER (Energy Efficiency Ratio) significantly. Comparing the fan power for fouled conditions to the fan power for clean conditions, the variation ranged from approximately –7% to a value as high as 40%.

From the literature survey it clear that there does not exist any study on the effect of fouling when using low GWP HFO refrigerants. Accordingly in this paper the system performance is computed on the basis of combined first law (Energy analysis) and the second law (Exergy analysis) of thermodynamics under fouled conditions for HFO1234yf and HFC134a. The effect of variation in evaporator conductance and condenser coolant inlet temperatures has been examined on the performance of the system. The parameters computed are COP, cooling capacity, compressor work and second law efficiency.

2. Model Descriptions

The schematic and T-S diagrams of vapour compression system/cycle are shown in figures 1 and 2 respectively.



–Figure 1: Schematic diagram of a simple VCRS

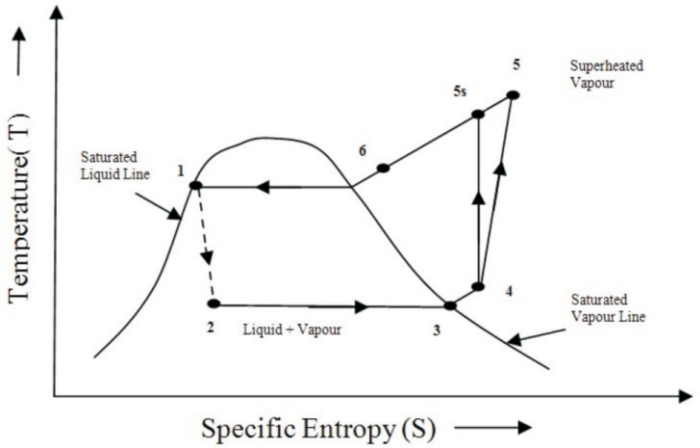


Figure 2: Temperature – Entropy diagram of VCRC

The various processes occurring in vapour compression cycle

I) Process 4-5s: Isentropic compression of the vapour from state 4 to 5s. However the compression is never isentropic and hence in actual compression process (4-5) the exit state from the compressor is 5.

ii) Process 5-6: Heat rejection at constant pressure to the surrounding from the discharge line.

iii) Process 6-1: Heat rejection in condenser at constant pressure.

iv) Process 1-2: An irreversible adiabatic expansion of vapour through the expansion valve or throttling device. The pressure and temperature of the liquid are reduced. The process is accompanied by partial evaporation of some liquid. The process is shown by dotted line because it is irreversible.

v) Process 2-3: Heat absorption in evaporator at constant pressure. The final state 3 the refrigerant is in the dry saturated state at the exit from the evaporator.

vi) Process 3-4: The temperature at the exit is lower than the ambient temperature hence heat is transferred from surroundings to the refrigerant in the suction line at constant pressure.

Considering the steady-state cyclic operation and applying the first law of thermodynamics to the system as shown in Figure 2, the equation (1) can be obtained as under:

$$\dot{Q}_{cond} + \dot{Q}_{loss,\,cond} - (\dot{Q}_{evap} + \dot{Q}_{loss,\,evap}) - \dot{W}_{cp} = 0 \quad (1)$$

The heat-transfer rate in the evaporator is given by:

$$\dot{Q}_{evap} = \dot{m}_{ref}(h_3 - h_2) \quad (2)$$

In terms of effectiveness (ϵ), minimum heat capacity (C_{min}) and temperature difference Q_{evap} can be written as

$$\dot{Q}_{evap} = (\epsilon C_{min})_{evap}(T_7 - T_2) \quad (3)$$

Where T_2 is the temperature of refrigerant entering to evaporator and T_7 is the outside air temperature entering to evaporator.
Similarly, the heat-transfer rate in the condenser is given by

$$\dot{Q}_{cond} = \dot{m}_{ref}(h_6 - h_1) = (\epsilon C_{min})_{cond}(T_1 - T_9) \quad (4)$$

Where T_1 is the temperature of saturated liquid refrigerant leaving the condenser and T_9 is the outside air temperature entering the condenser for cooling the refrigerant in the condenser.
The power required by the compressor is presented in terms of isentropic efficiency of the compressor, given by

$$\dot{W}_{cp} = \dot{m}_{ref}(h_5 - h_4) = \frac{\dot{m}_{ref}(h_{5s} - h_4)}{\eta_{cp,isn}} \quad (5)$$

Where point 5 shows the actual state of refrigerant vapour at the exit from compressor.
Work input to the compressor can also be expressed using steady flow energy equation as under:

$$\dot{Q}_{cp} - \dot{W}_{cp} = \dot{m}_{ref}(h_5 - h_4) \quad (6)$$

Where Q_{cp} is the heat transfer from the compressor to the surrounding.
The heat leaking into the suction line is represented by

$$\dot{Q}_{sl} = \dot{m}_{ref}(h_4 - h_3) \quad (7)$$

The heat leakage from the discharge line to surrounding can be expressed as

$$\dot{Q}_{dl} = \dot{m}_{ref}(h_6 - h_5) \quad (8)$$

The heat leakage from the discharge line to surrounding can be expressed as

$$COP = \frac{Q_{evap}}{W_{cp}} \quad (9)$$

The COP is the ratio of refrigerating effect to compressor power, i.e.
The first law efficiency alone is not a realistic measure of performance of engineering device. To overcome this deficiency, we define second-law efficiency (η_{II}) of a refrigeration system which is the ratio of the actual coefficient of performance (COP) to the maximum possible coefficient of performance (COP_{rev}) under the same operating conditions.

$$\eta_{II} = \frac{COP}{COP_{rev}} = \frac{\eta_I}{\eta_{th,rev}} \quad (10)$$

$$\text{Where, } COP_{rev} = \frac{T_7}{T_9 - T_7} \quad (11)$$

The effectiveness of a heat exchanger

is defined using equation (12) as under

$$\epsilon = \frac{\text{Actual heat transfer}}{\text{maximum possible heat transfer}} \quad (12)$$

The effectiveness of evaporator and condenser is given by equation 13 and 14

Incropera et al. [9] derived the expression for relation between effectiveness, heat capacity and overall conductance (UA) which is expressed as (14)

$$\epsilon_{evap} = \frac{T_7 - T_8}{T_7 - T_2} \quad (13)$$

$$\epsilon_{cond} = \frac{T_{10} - T_9}{T_6 - T_9} \quad (14)$$

The fouling on air side of a heat exchanger is the reason for reduction of UA. The percentage reduction in

$$UA = C_{min} * ln\left(\frac{1}{1-\epsilon}\right) \quad (15)$$

conductance is represented using the equation (16).

$$UA\% = \left(1 - \frac{UA}{UA_{cl}}\right) * 100 \quad (16)$$

The above methodology is used to develop a program, for performance computation, in Engineering Equation Solver (EES).

3. Results And Discussion

The thermodynamic model given above is used to evaluate the performance of vapour compression system. The performance is evaluated with two refrigerants (R134a and R1234yf).

Input conditions

Table 1: Values of inputs at design point.

Parameters	Values
Inlet Evaporator coolant temperature ($T_{in,evap} = T_7$ in K)	273
Inlet Condenser coolant temperature ($T_{in,cond} = T_9$ in K)	308-313
Cooling Capacity (Q_{evap} in kW)	100
Product of condenser effectiveness and capacitance rate of external fluid [$(\epsilon C_{min})_{cond}$, kW/K]	9.39
Product of evaporator effectiveness and capacitance rate of external fluid [$(\epsilon C_{min})_{evap}$, kW/K]	8.2
Isentropic efficiency of compressor ($\eta_{□□,□□}$)	0.65
Effectiveness (Є)	0.80
Refrigerants	R134a and R1234yf

The values given in table 1 are used for computation of results in current work.

Effect of evaporator fouling (evaporator conductance for R134a) on percentage change in compressor power, cooling capacity and COP

Figures 3, 4 and 5 represent the effect of evaporator fouling with variation in condenser coolant temperature for the refrigerants R134a and R1234yf respectively. It is observed that with increase in evaporator fouling the compressor power, cooling capacity and COP decreases.

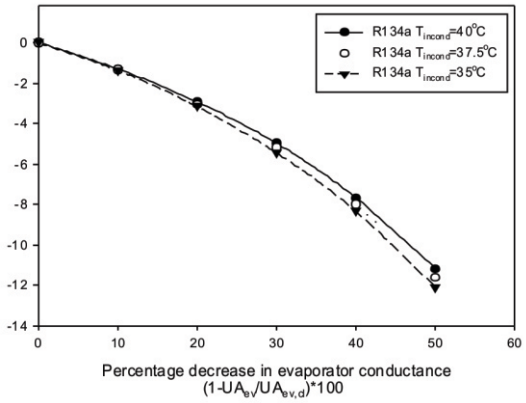


Figure 3: Percentage change in cooling capacity v/s percentage decrease in evaporator conductance for R134a.

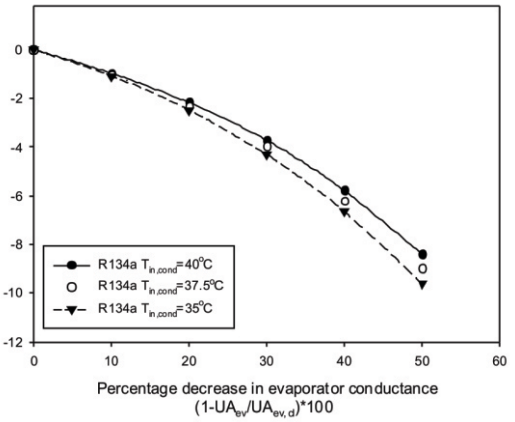


Figure 4: Percentage change in compressor work v/s percentage decrease in evaporator conductance for R134a.

The effect of evaporator fouling with variation in condenser coolant temperature decreases the COP, because with percentage decrease in evaporator conductance ((1-$UA_{ev}/UA_{ev,cl}$)*100), cooling capacity and compressor work both decrease. However the cooling capacity decreases at a higher rate as compared to compressor work.

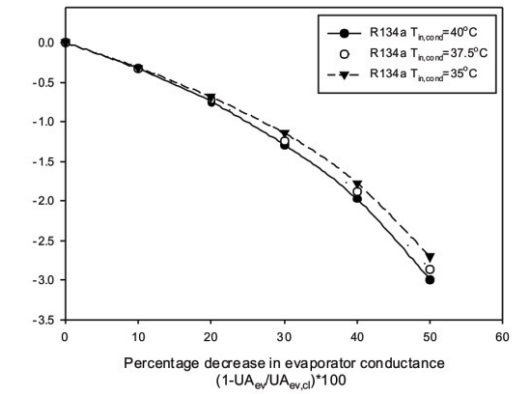


Figure 5: Percentage change in COP v/s percentage decrease in evaporator conductance for R134a.

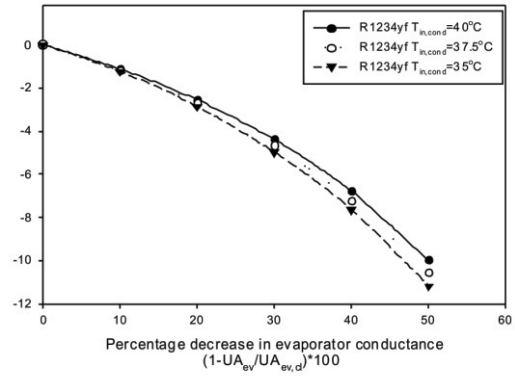


Figure 6: Percentage change in cooling capacity v/s percentage decrease in evaporator conductance for R1234yf.

Figures 6, 7 and 8 show the variation of percentage changes (%) in Q_{evap}, W_{cp}, and COP with percentage decrease in evaporator conductance for R1234yf.

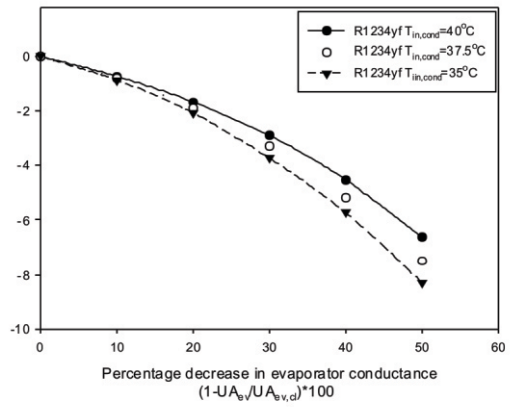


Figure 7: Percentage change in compressor work v/s percentage decrease in evaporator conductance for R1234yf

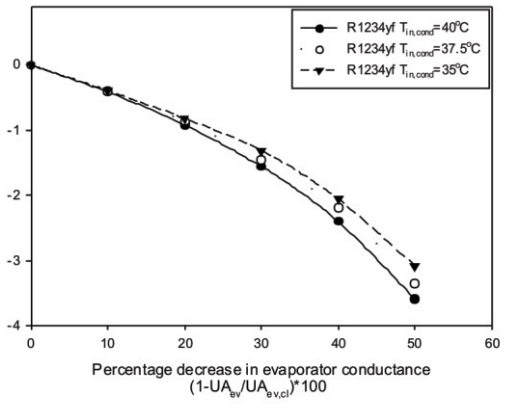


Figure 8: Percentage change in COP v/s percentage decrease in evaporator conductance for R1234yf.

The trends are similar in figures 6 to 8 for R1234yf when compared with the results of R134a shown in figures 3 to 5; hence it does not require explanation. The percentage decrease in the values of cooling capacity and compressor power is more in case of HFC134a as compared to HFO1234yf. However the percentage decrease in COP for HFO1234yf is more than HFC134a. The decrease in value of COP for R1234yf is 3.59% and for R134a is 2.99%.

Figures 9 and 10 show the variation of second-law efficiency (η_{II}) %, with evaporator fouling from 0% to 50%, at $T_{in,cond}$ = 40°C, 37.5°C, 35°C, for refrigerants R134a and R1234yf.

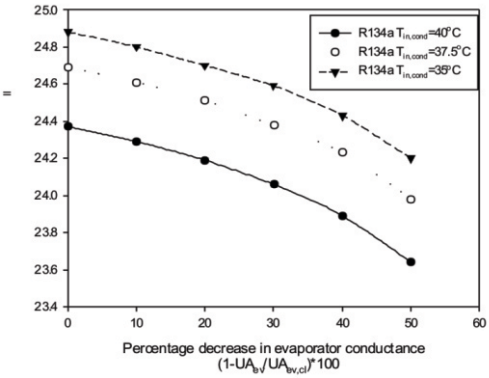


Figure 9: Second-law efficiency (%) v/s percentage decrease in evaporator conductance for R134a.

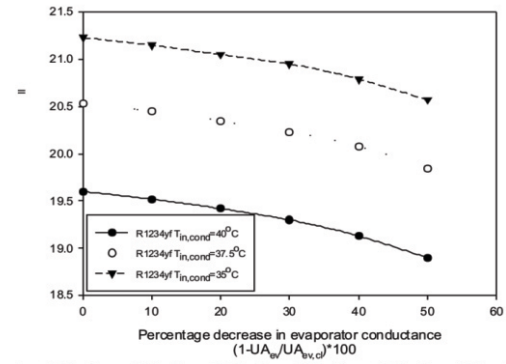


Figure 10: Second-law efficiency (%) v/s percentage decrease in evaporator conductance for R1234yf.

The comparison of the result of second – law efficiency at condenser inlet temperature of 40℃, 37.5℃, & 35 ℃ for unfouled condition & 50% reduction in evaporator conductance due to fouling are shown in Table 2.

Table 2 : Comparison of second-law efficiency (evaporator under fouled condition) for Refrigerant R1234yf with R134a.

Refrige-rant	Change in UA_{evap} (%)	η_{II} (%) $T_{in,cond}$ =40°C	η_{II} (%) $T_{in,cond}$ =37.5°C	η_{II} (%) $T_{in,cond}$ =35°C
R1234yf	0	19.60	20.53	21.23
	50	18.90	19.84	20.57
R134a	0	24.37	24.69	24.88
	50	23.64	23.98	24.20

From the above table it is clear that, the second-law efficiency for R1234yf is about 5-6% lower than R134a under clean as well as fouled condition.

Conclusions

On the basis of results obtained from thermodynamic model, following conclusions are drawn-

Effect of fouling on the performance of a simple vapour compression cycle has been evaluated by varying condenser coolant inlet temperature $T_{in,cond}$ (i.e. 35℃, 37.5 ℃ and 40℃), and also by varying evaporator conductances (i.e. 0% - 50%), for the refrigerant R134a and R1234yf.

In evaporator fouling it has been observed that:-

It is observed that the evaporator fouling has larger effect on cooling capacity (*Q*evap%) as it decreases by 12.08 for R134a and 11.19 for R1234yf. The compressor power (Wcp%) also decreases by 9.63 for R134a and 8.31 for R1234yf. The maximum percentage decrease in value of COP for R1234yf and R134a is 3.59 and 2.99 respectively. The second-law efficiency is also observed to decrease with decrease in the evaporator conductance for both Refrigerants (R134a and R1234yf).

References

[1] Calm, J., 2008. The next generation of refrigerants – Historical review, considerations, and outlook. *International Journal of Refrigeration* 31: 1123-1133.

[2] Ding, G., 2007. Recent development in simulation techniques for vapour-compression refrigeration systems. *International Journal of Refrigeration* 1-15.

[3] Cabello, R., J., Navarro and E., Torrella, 2005. Simplified steady-state modelling of a single stage vapour compression plant Model development and validation. *Applied Thermal Engineering* 25, 1740–1752.

[4] Lee, Y., and D. Jung, 2011. A brief performance comparison of R1234yf and R134a in a bench tester for automobile application. *Applied Thermal Engineering* 35: 240-242.

[5] Jarall, S. 2012. Study of refrigeration with HFO-1234yf as a working fluid. *International Journal of Refrigeration* 35: 1668-1677.

[6] Reasor, P., V., Aute, and R. Radermacher. 2010. Refrigerant R1234yf Performance Comparison Investigation. *International Refrigeration and Air Conditioning Conference* at Purdue University Paper No.1085.

[7] Ahn, Y., S., Cheong, Y., Jung, and J., Lee, 2006. An Experimental Study of the Air-Side Particulate Fouling in Fin-and-Tube Heat Exchangers of Air Conditioners. *International Refrigeration and Air Conditioning conference* at Purdue University Paper No. 818.

[8] Yang, L., J., E., Braun, and E., A., Groll, 2004. The Impact of Evaporator Fouling on the Performance of Packaged Air Conditioners. *International Refrigeration and Air Conditioning Conference* at Purdue University Paper No. 687.

[9] Incropera, F.P., D.P. DeWitt, T., Bergman, and A. Lavine. 2006. *Fundamentals of Heat and Mass Transfer*. New York: John Wiley & Sons.

Storage Stability of Biodiesel: A Review

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Abstract

Global warming, a spurt in population growth and an increase in demand for transport fuels in developing economies, all coupled together with limited reserves of fossil fuels, are realities that have convinced many countries of the need to develop alternative and renewable energy sources such as biofuels. Biodiesel is considered to be apromising alternative biofuel. Recently, biodiesel has received additional attention and intense research has been performed in this field all over the world due to its lower environmental impact compared to the conventional diesel fuels.The main problem of using biodiesel as fuel is its poor stability characteristics. Poor stability leads to gum formation which further leads to a storage problem of these fuels for a longer period of time. Oxidative degradation occurs in biodiesel on aerobic contact during storage as well as with metal

contaminants. Antioxidants are very effective for the eradication of those oxidation stability problems. This article presents an overview of the factors affecting the oxidation stability of biodiesel and the methods available for the prediction of oxidation stability. The effect of antioxidants in preventing the oxidation of biodiesel is also discussed.

***Key Words**: Biodiesel; Oxidative stability; Stability parameters; Antioxidants*

Inroduction

Stability is one of the important criteria concerning fuel properties. The stability of biodiesel is lower than common diesel fuel. The formation of deposits and gum and the darkening of fuels as a result of the formation of contaminants, such as alcohols,acids, aldehydes, peroxides, etc., occur during long-term storage of biodiesel fuel [1-2]. Various processes, including oxidation in aerobic conditions, hydrolysis in the presence of moisture, thermal decomposition by excess heat, contamination of impurities, etc., account for the instability of biodiesel that can change the fuel properties considerably [4-5]. Among these processes, oxidation is one of the significant stability concerns associated with bio diesel because it has a lower resistance capacity to oxidation and can easily be affected by air oxidation during long-term storage [3]. The composition of the fatty acid portion of the biodiesel ester molecule is the most important factor that affects its properties. The composition varies based on the feedstock used for biodiesel production. When compared to diesel fuel, the unsaturation in the molecule accounts for biodiesel instability. As the unsaturation in the fatty acid chain portion increases, the biodiesel becomes more unstable. Oxidation starts at the allylic positions to double bonds. Therefore, the fatty acid composition of the ester, especially the position of and the number of allylic and bis-allylic methylene moieties adjacent to the double bond, determines the rate of oxidation. In Fig. 1, the positions in the oleic acid,

linoleic acid and linolenic acid (most common unsaturated acids present in the oils or fats and thus in the biodiesel) that are vulnerable to oxidation are highlighted by a circle with dotted lines. The allylic and bis-allylic methylene moieties are the most susceptible to oxidation as a result of the radical chain reaction [3].The oxidative degradation during long-term storage occurs mainly in the presence of air, heat, light and pro-oxidants [1-3]. Biodiesel oxidation is of two typesauto-oxidation and photo-oxidation. Auto-oxidation is a major cause of biodiesel oxidation. The auto-oxidative degradation of biodiesel is a radical chain reaction and involves initiation, propagation, and termination steps. During the initial stages of biodiesel oxidation, the methylene groups allylic and bis-allylic to the double bonds are more active and hydrogen radicals are abstracted by radical initiatorsThe resultant radicals interact with oxygen, which results in peroxide formation for the propagation step. The peroxides propagate the chain reaction by the further abstraction of hydro- gen from the methylene moieties and form carbon radicals and hydro peroxides. Next, the newly formed carbon free radicals will again combine with oxygen and continue the propagation process. This chain process continues until the termination step, which provides the formation of stable products the hydro peroxide formation during the auto-oxidative degradation of linoleic acid methyl ester. The ultimate decomposition of peroxides results in the formation of aldehydes, such as hexenals [1,18]. At high temperatures, highly stable conjugated structures are formed by the isomerization of methylene-interrupted polyunsaturated olefin units. For the isomerisation process, one of the conjugated diene groups in the chain can react with the olefinic group from the nearby fatty acid chain and can form a substituted cyclohexene ring from the Diels alder reaction. At high temperatures of 180 ^{0}C, thermal dimerization occurs for the fatty acid methyl ester due to the Diels Alder reaction and forms the dimer. shows the cyclohexene ring formed from linoleic acid methyl ester and illustrates the formation of dimers via the Diesel Alder reaction of linoleic

acid methyl esters. The same reactions can also occur during the frying process of oil or fat and can adversely affect the performance of biodiesel obtained from used cooking oil or animal fat. The fatty acid compositions (mass%) of several biodiesel feed- stocks are given among the different feedstock shown in, coconut oil has a small amount of unsaturated fatty acid (9%) and may be less susceptible to oxidation. Addition- ally, feedstock with more unsaturated fatty acid part may have more bis-allylic hydrogen and may generate less stable biodiesel. Among the different feedstock given in the table, linseed oil (with 53% linolenic acid) may have the highest tendency for oxidation based on its fatty acid composition. Most of the parameters affecting the oxidation stability also depend on the fatty acid composition of the ester.

2. Parameters Indicating the Extent of Oxidation Stability of Biodiesel

An understanding of selected fuel parameters is highly important in evaluating the oxidation stability of biodiesel. Most of those parameters are directly related to the fatty acid composition of the biodiesel ester molecules. The important parameters that help to predict the oxidation stability of a biodiesel sample, their determination and its effect on the oxidation of biodiesel are discussed below.

2.1 Iodine value (IV)

The estimation of the IV for biodiesel fuel, which is the measure of the total degree of unsaturation, provides useful guidance for preventing various problems in engines. The IV is based on the reactivity of alkyl double bonds, and an increased IV of biodiesel indicates the possibility for the formation of various degradation products that can negatively affect engine operability and reduces the quality of lubrication [1]. The IV is expressed as the gram of iodine consumed per 100 g of the substance, which is the most parameter employed for determining the magnitude of unsaturation in the esters of fatty acids, fats, oils and their derivatives [1-4]. The local and international standard organisations provided procedures for the

determination of IV in biodiesel. The IV indicates the tendency of biodiesel to oxidise or polymerise, which leads to the formation of insoluble sediments. An increase in the degree of unsaturation causes an increase in the iodine used. The IV considers that the nature, position in the chain and the amount of oleniccarbons in the fatty compounds are equal and thus equally reactive, which makes the IV not able to distinguish the structural differences that are present in different fatty compounds [3]. Therefore, the IV does not provide a measure to determine whether the hydrogens are allylic or bis-allylic to the double bonds, which is an important factor for determining the oxidisability of biodiesel. Biodiesel stability is not related to the total number of double bonds expressed by the IV but is mainly related to the number and position of the bis-allylic methylene moieties adjacent to the double bond.

2.2 Induction period (IP)

Biodiesel oxidation is mainly the result of a radical chain reaction that causes the formation of hydro peroxides. During the initial period of storage, the formation of hydro per- oxides is very low. This dead time will vary based on the nature of the FAME, the presence of additives, the conditions of storage, etc. This characteristic time period is called the induction period (IP). The relative oxidation rate study of the methyl esters conformed that biodiesel with more poly-un-saturations in the sample can easily experience oxidation [5]. The oxidation rate of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids is noted as 1:12:25. Additionally, the stability predicting parameter, called the oxidation stability index, is related to the IP. The minimum IP limits, which are specified by the American (ASTM D6751-11b) [1] and European (EN 14214) [26] standards for biodiesel in the resistance of oxidation, are 3 h and 6 h, respectively. The Indian speciation IS-15607 recommends a minimum of 6 h as the induction time

2.3 Peroxide value (PV)

The PV is generally based on the primary oxidation products, such as the hydro peroxides of the biodiesel, and is a measure of the peroxide units

formed during the oxidation process. The PV is measured in mill equivalents of peroxide units per kg of the biodiesel sample. The PV influences various parameters in the fuel standard, such as the cetane number (CN), density, viscosity, etc. [13]. The increase in PV increases CN, which may reduce the ignition delay time [12]. The increase in PV as well as the acidity after the IP can also cause the corrosion of the fuel system components, the hardening of the rubber components, the fusion of the moving components and engine operation problems Several studies exist for storage stability tests for biodiesel, which show that oxidation can affect fuel quality with respect to the PV [15] report that a low PV is required for the high stability of biodiesel against oxidation. [1] haveanalyzed the PV of karanja oil methyl ester (KOME). According to the results obtained from the 180-day storage study, the PV increased as the storage time of biodiesel increased. Therefore, oxidation stability decreases with an increase in storage time.

2.4 Viscosity

Lower atomization characteristics in the fuel injector are the result of higher viscosity and create many severe effects on engine performance [7-8].The blending of biodiesel is an effective method for improving the properties at low temperatures [9-12].Because the vaporization and atomization of the fuel is reduced as a result of the high viscosity of the fuel, the fuel requires the viscosity of biodiesel increases with an increase in the carbon chain length, the degree of saturation of the fatty acid and its ester and the presence of free fatty acids. The viscosity of the biodiesel obtained from the used cooking oil is higher than the biodiesel obtained from neat vegetable oils. Samples with cis double bond configurations have lower viscosity, whereas samples with trans double bonds have higher viscosity. However, the position of the double bond has a minor effect on the viscosity .Highly viscous samples also have a high tendency for oxidation. The main reason for the rapid oxidation processes with a high viscosity is due to the isomerization of the double bond, usually cis to trans,

along with the formation of high molecular weight products. Viscosity is useful for the measurement of the oxidation progression of biodiesel. The polymeric secondary oxidation products of biodiesel cause the formation of soluble gums and insoluble sediments and will result in an increase in the viscosity.

3. Methods Used to Predict the Stability of Biodiesel

A wide variety of techniques have been used for the stability determination of fatty acid esters. The type of test method depends mainly upon the nature of the stability, including thermal stability, oxidation stability and storage stability. For the determination of thermal stability, the Rancimat test, ASTM D6408-08 and TGA/DTA are used. For the storage stability determination, a modified Rancimat test, ASTM D4625-04, and ASTM D5304-06 are used. The Active Oxygen Method (AOM), ASTM D2274, ASTM D3241, EN 14112, and ASTM D5483 are the methods used for the oxidation stability determination of biodiesel.

3.1 ASTM D4625-04

The ASTM D4625-04 method is the most widely established method for the estimation of storage stability for the middle distillate petroleum fuels [1]. In this method, the fuel is stored at a temperature of 43 1C for a period of time, such as 24 weeks. The sample is then filtered to evaluate the insoluble sediments of the sample, and the remaining filtrate was investigated to deter- mine the total AV and kinematic viscosity. These tests must be carried out weekly. For the precipitation of polar polymers present in the sample, isooctane is added. This modification is necessary in cases where soluble products are formed by the oxidation [1-3]. Because the temperature in the test conditions is slightly higher than room temperature, fuel oxidation and other degradative reactions lead to the formation of sediment that is mildly accelerated in this method when compared with typical storage conditions. In this method, the storage stability prediction is more reliable than the other more accelerated tests. However, because the storage periods are lengthy (4–24 weeks), the test method is not appropriate for quality

control testing and only provides a tool for research on the storage properties of fuels. The storage material is also an important aspect for this study.

3.2 ASTM D6468-08 – Light Reflectance Method

For the high temperature stability determination of the middle distillate fuels (including biodiesel), the ASTM D6468-08 method is more prominent [1]. Here, the sample is aged at 150C in open tubes with air contact for approximately 90 or 180 min. After the aging process, the sample is cooled and the insoluble sediments are filtered and estimated by the light reflectance method of the filter paper. For comparison purposes, a blank is conducted without the sample using an unused filterpad [6]. The filter paper used for this ASTM method has a nominal porosity of 11 μm, and thus, it cannot capture all of the sediment formed during aging, although it allows differentiation over a broad range of particle sizes for the sediments. The method of reflectance measurements can be affected by the colour of the filterable insoluble and may thus not be successfully correlated to the mass of the material that is filtered. Thus, the accuracy of the method is not 100%. This method can provide an estimate of the stability of fuel when exposed to high temperatures in situations, including a recirculating engine or burner fuel delivery system, and under other high temperature conditions with limited exposure to air. In addition, the test method is also helpful in the study of operational problems related to fuel thermal stability. This method is not suitable for fuels whose flash point is less than 38 1C. This test method is also not suitable for fuels containing residual oil and is thus only suitable in the estimation of the high temperature stability of biodiesel with a very high FAME content.

3.3 ASTM D2274 – Gravimetric Analysis

This method is based on the filtration, which is followed by the gravimetric analysis of the insoluble materials that are formed by the oxidation in the presence of heat. Here, the sample is first aged at 95 C for 16 h by the bubbling of oxygen at a rate of 3 L/h.

The insoluble sediments formed by the thermal oxidation stick on the oxidation cell and are detached with the help of a tri-solvent containing equal parts of toluene, acetone, and methanol. The solvent is then evaporated to recover the insoluble sediments (insoluble) formed. The total yield of the insoluble, expressed as milligrams per 100 ml, is reported as total insoluble. An additional analysis exists for the determination of biodiesel-soluble polymers. In this case, iso-octane is added to the sample so that the soluble polymers will precipitate. This precipitate is filtered to acquire the measure of the soluble polymers [1,3]. The use of an elevated temperature and a pure oxygen atmosphere for the test may cause differences in the nature and amount of insoluble formed in real storage situations. This test method is also not applicable to fuels containing residual oil. This test method has not been validated for the testing of biodiesel or blends of middle distillates and biodiesel meeting ASTM specifications. The test method D7462 is more suitable for testing B100 and all blends of middle distillates and biodiesel because samples containing biodiesel can cause a partial dissolution or compromise of the membrane filter, providing erroneous results.

3.4. EN 14112, Rancimat Method-IP measurement

The Rancimat method is the usual and the official method for determining the oxidative stability of oils and fats by the American Oil Chemists' Society (AOCS). In this method, the temperature range is usually limited to a maximum of 13 ^{0}C [1]. After that, air is bubbled through the sample so that the oxidation of the sample takes place. As a result of the oxidation process, a release of some gases along with the air occurs, which is then passed to deionized water in a flask. Theflask has an electrode, which is connected to a device for a measurement of the conductivity. The induction period (IP) is measured for this test method. Here, the IP is noted as the time at which the conductivity starts to increase very quickly. The continuous measurement of this conductivity gives an oxidation curve. The point of inflection of this curve is

known as the induction period. Volatile acidic gases, such as formic acid, acetic acid and some other acids, are produced by the oxidation and are absorbed in the water, which is the main reason for the increment in the conductivity and in the IP measurement [1,3].

3.5 Effect of Antioxidants on the Biodiesel Stability

It is evident from literature that higher concentration of antioxidants is more effective in radical trapping and hence minimize the extent of oxidation of a biodiesel. The increase in viscosity of the biodiesel sample over a period of time is an indicator of loss of stability i.e. this value provides an indication of the oxidative reactivity of a biodiesel. Both synthetic and natural antioxidants showed that they were able to retard the oxidation process and improve the storage stability.However, the synthetic antioxidant (BHT) showed better performance when compared to natural antioxidant. These results have clearly showed that the type of antioxidant and its dosage plays an important role in retarding auto oxidation of biodiesel during storage. The results of these experiments (acid value vs. time and viscosity vs. time) contributed to the development of a predictive model.[3]

3.6 Effect of Metal Contaminants and the Storage Container on the Stability of Biodiesel

The presence of metal contaminants is another reason for the deterioration of biodiesel during storage. Eduardo Pereyra mentioned about the storage materials for biodiesel [3]. Biodiesel undergoes an interaction with the metals, especially with Cu and its alloys, and as a result, insoluble sediments are formed in bulk quantities by the oxidation process. Among the different metals, Cu has the strongest catalyzing effect on the oxidation process. In addition, biodiesel is infused into plastic materials, such as ethyleneand polypropylene, during its contact [1,3]. Therefore, these plastic materials and Cu-containing tanks are not suitable for the storage of biodiesel. In the case of metals and alloys, the compatible ones include aluminium, carbon steel, stainless

steel and fibre glass [26]. Storage materials made up of copper, bronze, tin, zinc, etc. may hasten the oxidation of biodiesel and may result in the formation of insoluble sediments.

4. Conclusions

The biodiesel stabilitymay be affected by large number of parameters which can be categorized by oxidation, thermal and storage stability parameters. The present review has covered the different types of the fuel stabilities, mechanism of occurrence and correlations/equations developed to investigate the impact of various stability parameters on the stability of the fuel. Main parameters related to stability are PV, AV, IP, BAPE, APE, OSI and OX. And it was found that impact of APE is more on induction period than with that of BAPE. A review of the use of different types of natural and synthetic antioxidants has also been presented which indicates that natural antioxidants, being very sensitive to biodiesel production techniques and the distillation processes have varying impacts on the fuel stability. The work on the use of synthetic antioxidants on the stability of biodiesel fromvarious resources have indicated that out of various synthetic antioxidants studied so far only 3 antioxidants have been found to increase the fuel stability significantly. However, effectiveness of these antioxidants is if the order of TBHQ > PY >PG. The reviewreveals that, lot ofworkis requiredtobe done for stability of non-edible oils. Apart from this, additional research is required tobe done to investigate the effect of stability of biodiesel on engineperformance as well as effect on emissions.

References

[1] ZahiraYaakob, Binitha N. Narayanan , SilijaPadikkaparambil , Surya Unni K. , Mohammed Akbar P.A review on the oxidation stability of biodiesel,Renewable and Sustainable Energy Reviews(2014)

[2] Siddharth Jain, M.P. Sharma, Study of oxidation stability of Jatropha curcas biodiesel/ diesel blends, energy and environment

[3] A. Venkatram Kiran, J. Jayapriya &. Manoj Ravi (2015): Evaluation and Predictive Model

Development of Oxidative Stability of Biodiesel on Storage, Chemical Engineering Communications, DOI: 10.1080/00986445.2015.108538 3

[4] M. Balat and H. Balat, "Progress in biodiesel processing," Appl. Energy, vol. 87, pp. 1815-1835, 6, 2010.

[5] A. Pal, A. Verma, S S. Kachhwaha, S. Maji, Biodiesel production through hydrodynamic cavitation and performance testing. Renewable Energy, 35, 619(2010).

[6] Raheman, H., Phadatare, A.G. Diesel engine emissions and performance from blends of karanja methyl ester and diesel. Biomass Bioenergy, 27, 393–397, (2004).

[7] Shahidi F, Zhong Y. Lipid oxidation and improving the oxidative stability. ChemSoc Rev 2010;39:4067-79.

[8] Yadav, A.K..Khan, M.E. Dubey, A. M. Pal, A. Performance and emission characteristics of a transportation diesel engine operated with non-edible vegetable oils biodiesel, Case Studiesin Thermal Engineering 8(2016)236–244

[9] Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine

[10] A.K. Yadav et al., Kaner biodiesel production through hybrid reactor and its performance testing on a CI engine at different compression ratios, Egypt. J. Petrol. (2016), http://dx.doi.org/10.1016/j.ejpe. 2016.07.006

[11] Ryu K. The characteristics of performance and exhaust emissions of a diesel engine using a biodiesel with antioxidants. Bioresource Tech. 2010; 101: 578–582.

[12] Yadav, A.K., Khan, M.E., Pal, A., Sharma, D. Optimisation of biodiesel production from bitter groundnut oil using Taguchi method and its performance and emissions characteristics on a 4-cylinder Tata Indica engine', Int. J. Sustainable Agricultural Management and Informatics, Vol. 1, No. 4, pp.285–300,2015

[13] Rao TV, G. Rao P, K. Reddy HC.

Experimental investigation of 458 Pongamia, Jatropha and Neem methyl esters as biodiesel on c.i. engine. Jordan J Mech. and Ind. Eng. 2008;460 2(2):117 –22

[14]ChakrabortyM,BaruahDC.Investigationofoxidationstabilityof Terminaliabelericabiodiesel and its blends with petrodiesel. Fuel Process Technol 2012;98:51–8.

[15]Hiroaki Imahara, Eiji Minami, Shusaku Hari, Saka Shiro. Thermal stability of biodiesel in supercritical methanol. Fuel 2008;87(1):1–6.

[16]Bannister CD, Chuck CJ, Bounds M, Hawley JG. Oxidative stability of biodiesel fuel. ProcInst Mech Eng Part D:J Automob Eng 2011; 225:99–114.

[17]Santos NA, Cordeiro AMTM, Damasceno SS, Aguiar RT, Rosenhaim R, Filho JRC, et al. Commercial antioxidants and thermal stability evaluations. Fuel 2012;97:638-43.

[18] Xue, J., Grift, T.E.; Hansen, A.C. Effect of biodiesel on engine performances and emissions. Renew. Sustain. Energy Rev., 15, 1098–1116. (2011)

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