Transesterification of waste oil into biodiesel: Process Development, CFD simulation and Engine performance testing

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OUTLINE

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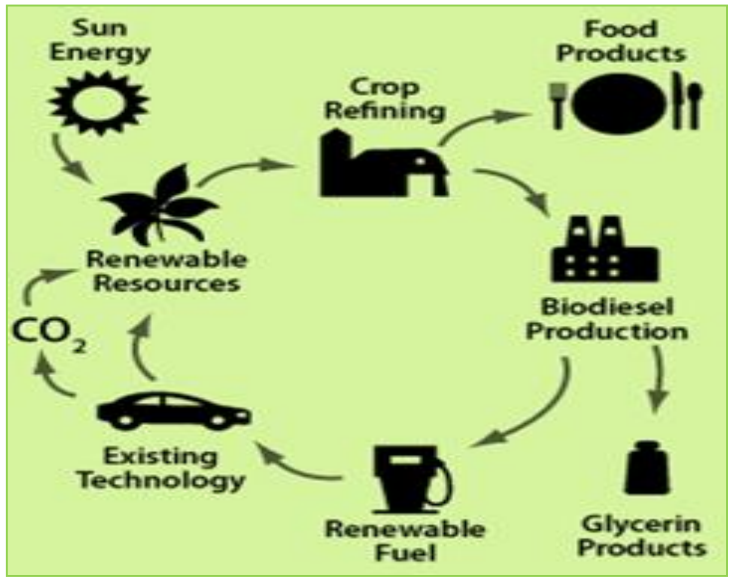
- Problem statement
- Objective
- Biodiesel overview
- Transesterificaton process
- Homogeneous base Transesterification via batch reactor
- Homogeneous base Transesterification via continuous process
- Numerical Simulation of Transesterification
- Engine emission testing
- Conclusion

PROBLEM STATEMENT

Environmental protection and conservation

Emissions



Waste

Abu Dhabi:
80 tons waste/day

Biodiesel

Lessen their negative environmental impact.

Establishing world class waste management systems

OBJECTIVE

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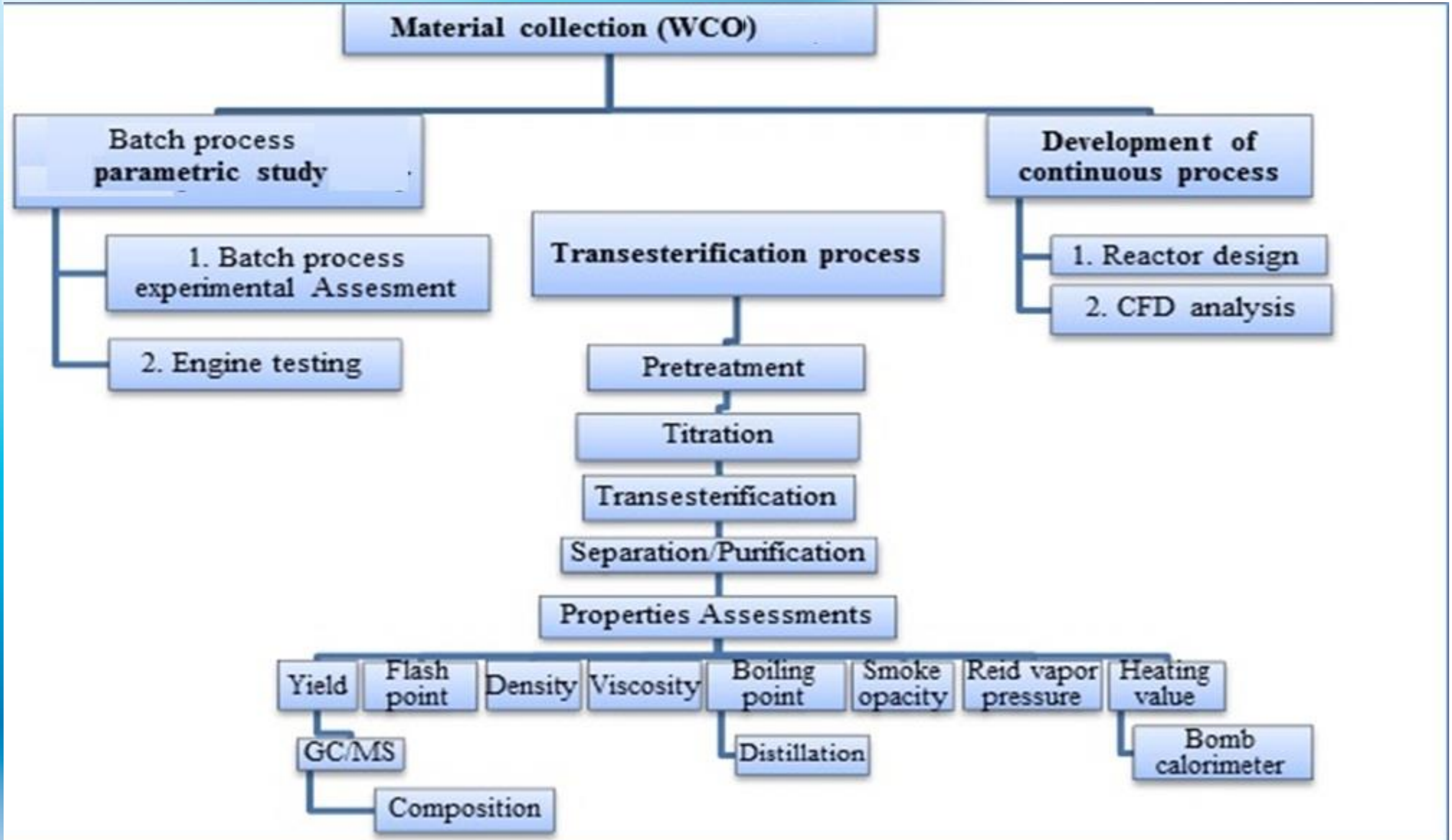
- Achieve optimal process metrics i.e. residence time, production configuration, biodiesel yield and catalyst choice. (Acceptable fuel properties within the ASTM Standards).
- Develop a continuous transesterification reactor following numerical simulation.
- Test the performance and emissions of diesel engine using different fuel blends

SCOPE OF WORK

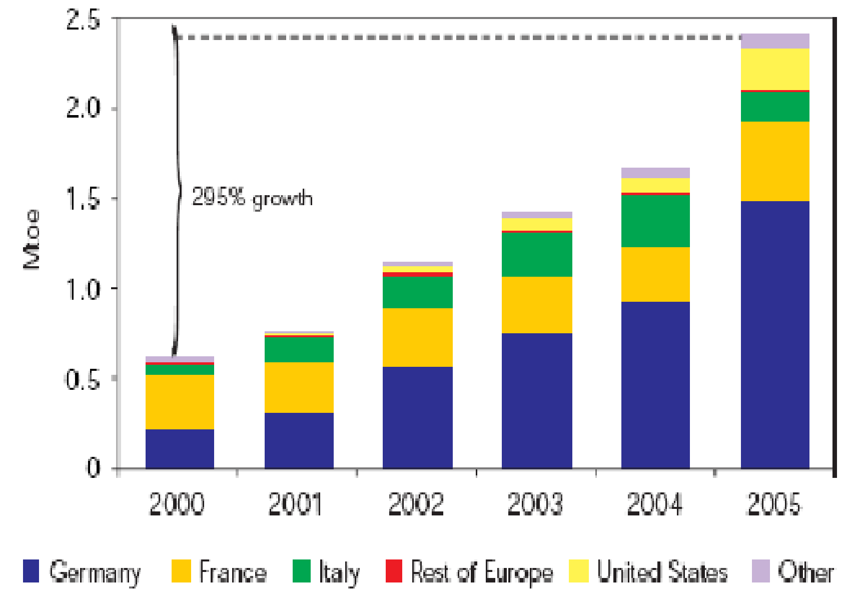


BIODIESEL OVERVIEW

What is Biodiesel?

- Mono alkyl esters derived from renewable sources
- Has comparable physical and chemical properties to petroleum diesel.
- Biodegradable, nontoxic, and renewable
  - Reduce GHG emissions and lower harmful emissions
- Variable feedstock sources including WCO

World production of biodiesel



Non-edible	Edible	Waste
Jatropha	Soybean	Waste cooking
Rapeseed	Palm	Tallow
Castor	Canola oil	Soap stock
Pongamia pinnata	Sunflower	Trap grease
Sea mango	Olive	
Seashore mallow	Olive	
Camelina		
Karanja		

TRANSESTERIFICATON OVERVIEW

What and why transesterificaton?:

- Triglyceride lipids reacts with alcohol using a catalyst to form alkyl esters and glycerol

$$Triglyceride + Alcohol \xleftrightarrow{catalyst} FAME + Diglyceride$$

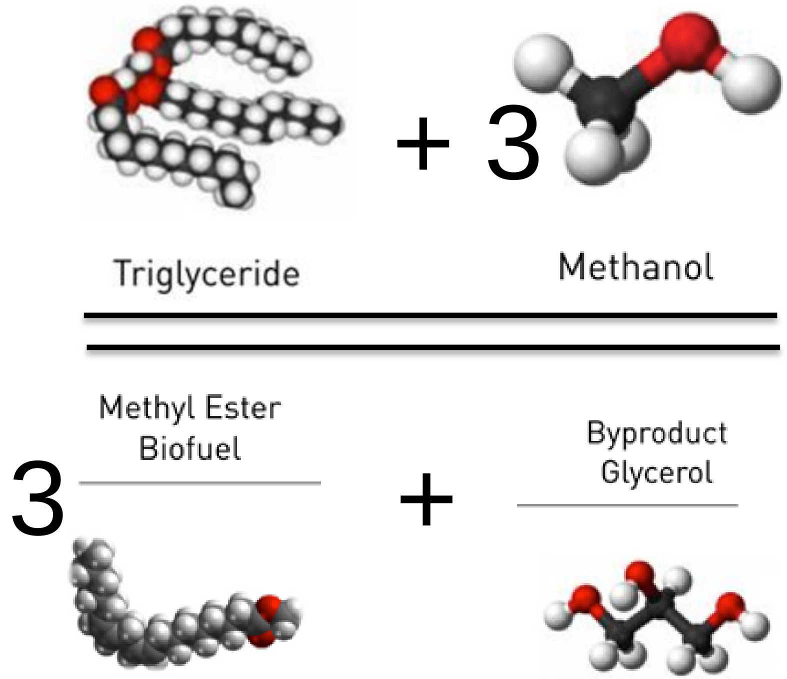
$$Diglyceride + Alcohol \xleftrightarrow{catalyst} FAME + Monoglyceride$$

$$Monoglyceride + Alcohol \xleftrightarrow{catalyst} FAME + Glycerol$$

$$FFA + Alcohol \xleftrightarrow{catalyst} FAME + H_2O$$

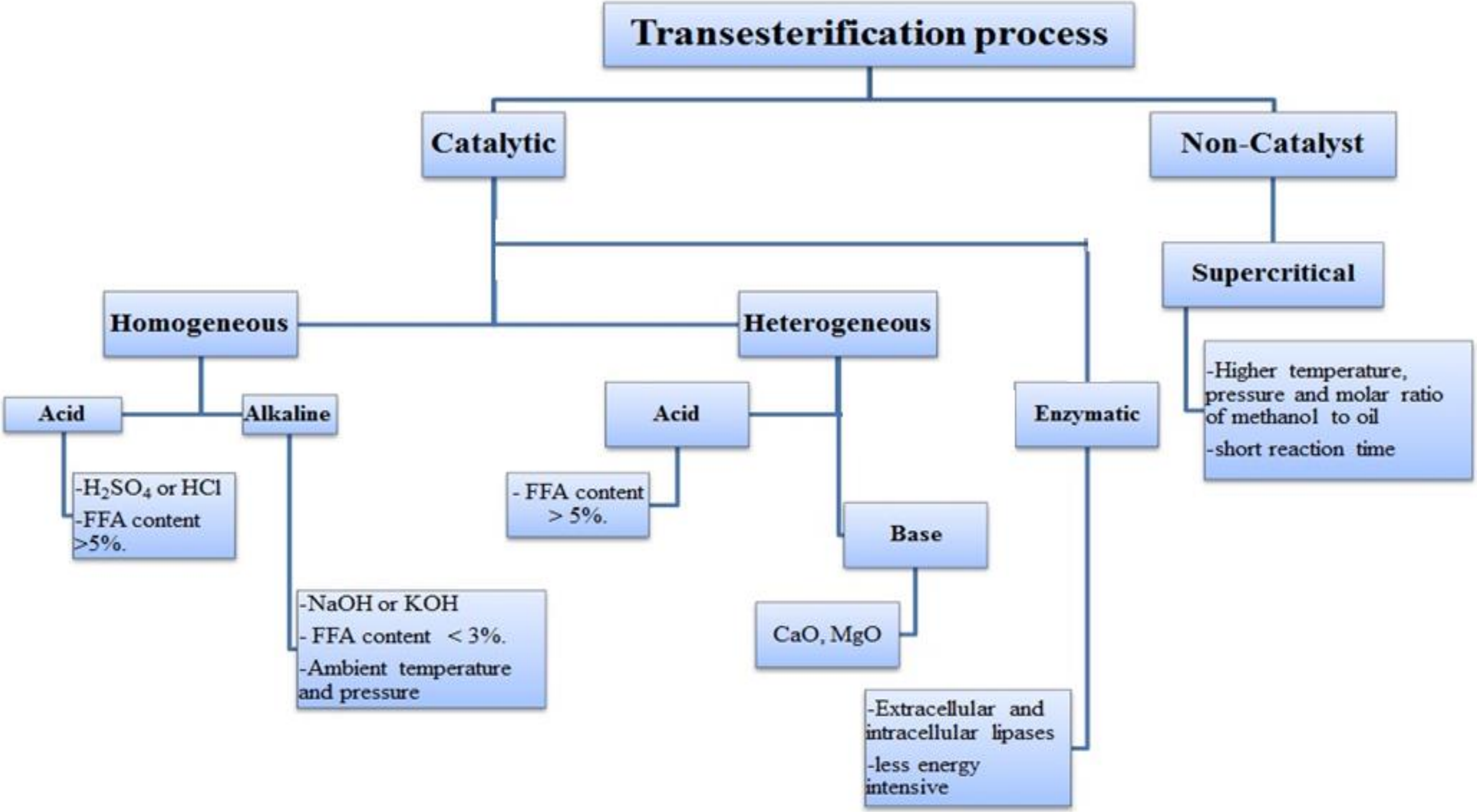
$$FFA + KOH \overset{r_2}{\longleftrightarrow} Soap + H_2O$$

$$Triglyceride + 3H_2O \longrightarrow 3FFA + Glycerol$$



- Superior lubricity and flashpoint, lower to no sulfur content, reduction in most exhaust emissions

Transesterification process



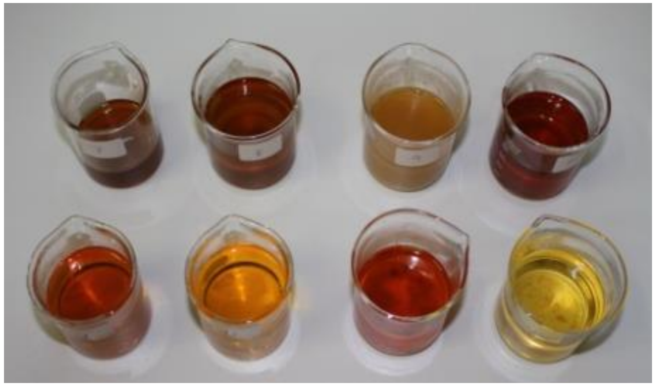
MATERIAL & METHODS

Raw material:

- Collection of WCO from local restaurants & School Cafeteria
- Pretreatment of WCO:
  - Solid removal: Filtration through a 15-20 μm filter
  - H_2O removal: Heating to 70-100 °C for one hour

Titration:

  - 5g of pretreated waste oil
  - 50ml of isopropyl alcohol,
  - 5 drops of phenolphthalein pH indicator.
  - Titrate 0.1 M NaOH solution added to the mixture.



- Evaluate acid value:

$$Acid\ value = \frac{Vol_{NaOH}\ (ml) \times Conc_{NaOH}(M) \times MW_{KOH}}{Sample\ weight\ (g)}$$

HOMOGENEOUS BASE TRANSESTERIFICATION

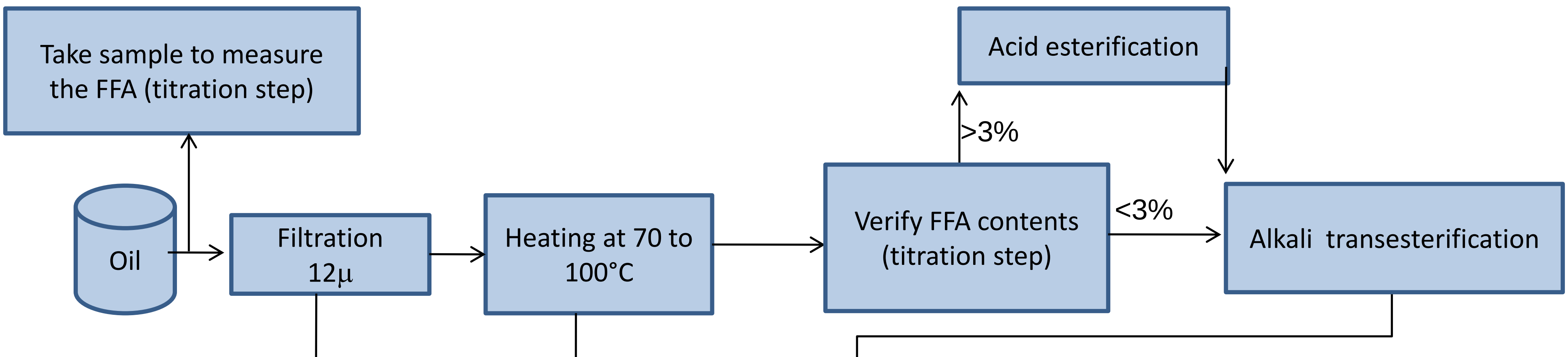
- Most commercial biodiesel transesterification processes are using a homogeneous alkaline catalyst
- Homogeneous alkaline vs. acid catalysts:
  - Faster reaction time
  - Less methanol consumption
  - Less aggressive and corrosive catalyst.

Catalyst	Benefits/Advantages	Drawbacks/ limitations
Alkali catalysts including • NaOH • KOH, • CH_3ONa • CH_3OK	• Least expensive • Simple to perform • Proceeds near condition	• Water content less than 0.05 wt.% • FFA content of less than 3%. • Complex separation and purification process

HOMOGENEOUS BASE TRANSESTERIFICATION MATERIAL & METHODS

Processing method:

1. Filtration and water removal;
2. FFA neutralization;
3. Catalyzed transesterification;
4. Separation and purification
5. Product assessment (ASTM);
   - Density and Vapor pressure;
   - Viscosity
   - Flash Point;
   - Distillation, boiling, T90



HOMOGENEOUS BASE TRANSESTERIFICATION VIA BATCH REACTOR

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Design of Experiment:

- Factors influence the transesterification process:
  - **3Tees,** i.e. Reactor configuration
  - Molar ratio of alcohol to oil
  - Amount & type of catalyst

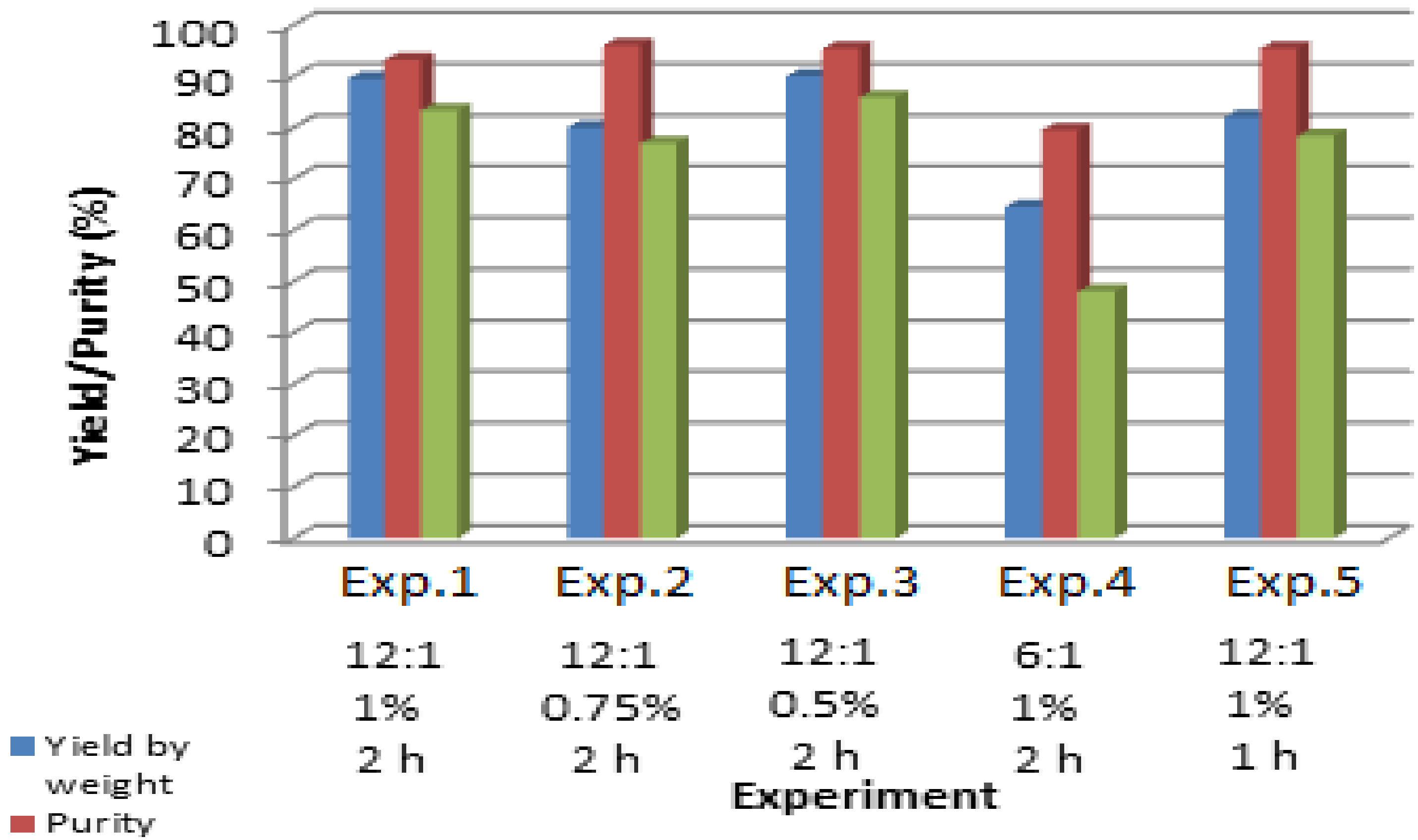
- Study different WCO to alcohol ratios and catalyst conct. at T=60ºC and 400 rpm

Exp.	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Time (hours)
Exp.1	Methanol	12:1	NaOH	1	2
Exp.2	Methanol	12:1	NaOH	0.75	2
Exp.3	Methanol	12:1	NaOH	0.5	2
Exp.4	Methanol	6:1	NaOH	1	2
Exp.5	Methanol	12:1	NaOH	1	1

VK 7010 dissolution apparatus, used as multiple bioreactors

RESULTS & DISCUSSION

FAME (biodiesel) Yield and Purity:



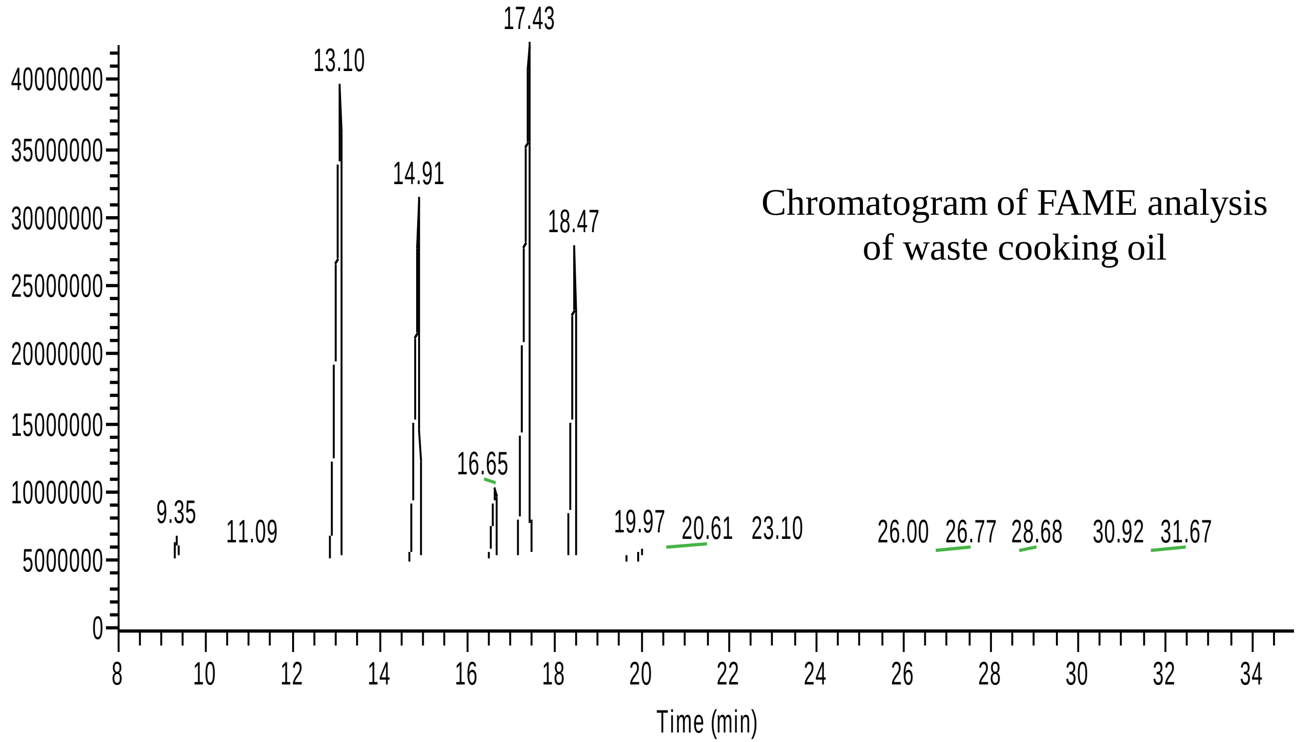
Biodiesel yield in alkaline homogeneous (NaOH) catalyst transesterification of WCO using methanol

RESULTS & DISCUSSION

FAME (biodiesel) Chromatogram analysis :

Fatty acid methyl ester (FAME) profile (relative %) WCO biodiesel.

FAME	WCO FAME
C14=Myristic acid	1.2
C16= Palmitic acid	36.9
C18:0 = Stearic acid	6.7
C18:1= Oleic acid	31.6
C18:2= Linoleic acid	18.9
C20= Arachidic acid	0.7
C20:1= Gadoleic acid	0.3
C22= Behenic acid	0.3



Chromatogram of FAME analysis of waste cooking oil

RESULTS & DISCUSSION

Evaluation of biodiesel properties: Temp at 60 °C and 500 rpm stirring

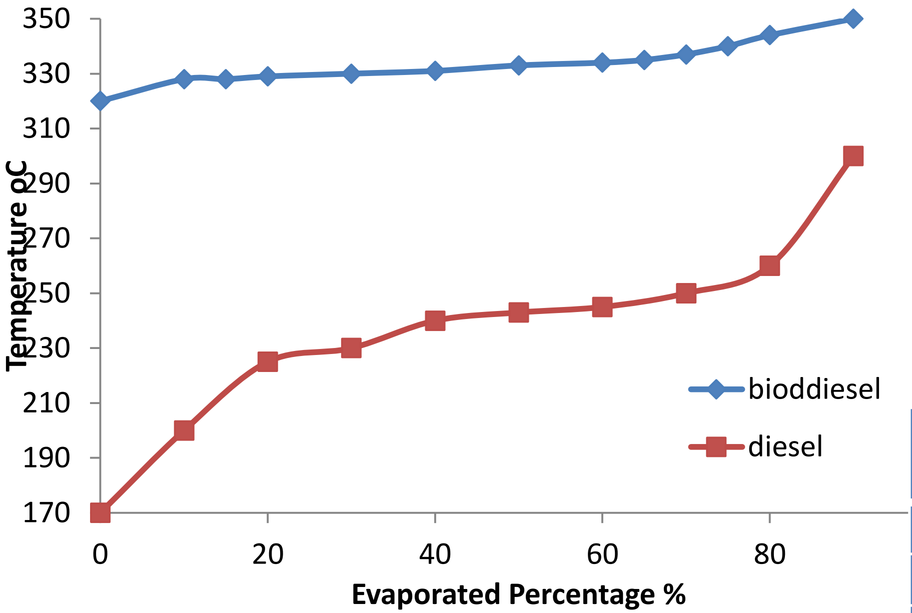
Exp.	Flash point (° C)	Density kg/m³	Viscosity (mm²/s)	Acid value (mg KOH/g)	Boiling point (° C)	T-90 ° C	Gross heating value MJ/Kg
Exp.1	177	890	4.64	0.79	326	338	40.180
Exp.2	182	843	4.65	0.67	320	346	40.357
Exp.3	179	839	4.72	0.45	320	352	40.137
Exp.4	163	838	4.68	0.73	322	347	40.396
Exp.5	157	842	4.63	0.84	318	340	40.223
Petro diesel	88	811	3.97	0.22	185	370	45.800

Fuel	Opacity Value (%) Assuming 100Hp setup			Opacity Value (%) Assuming 200Hp setup		
Biodiesel	1.4	1.3	1.3	1.9	1.4	1.4
Petroleum diesel	11	19.9	12.2	18.9	23.7	24.6

RESULTS & DISCUSSION

Biodiesel Distillation Curve

Volume %	0 1st drop	10	15	20	30	40	50	60	65	70	75	80	90
B. point (°C)	320	328	328.5	329	330	331	333	334	335	337	340	344	350



- Boiling points and weight fractions of alkane and alkene hydrocarbons in biodiesel
- 77.102wt% n-alkenes and 22.898wt% n-alkanes

Hydrocarbons	Boiling points °C	Density, ρ (g/ml)	Volume, V (ml)	V2-V1 (ml)	Mass=ρ *V (g)	Mass %
$C_{18}H_{36}$	320.0	0.789	0	0	0	0
$C_{19}H_{38}$	328.0	0.790	15	15	11.85	19.17
$C_{19}H_{40}$	330.0	0.786	30	15	11.79	19.07
$C_{20}H_{40}$	340.8	0.796	75	45	35.82	57.94
$C_{20}H_{42}$	343.0	0.789	78	3	2.367	3.83

Low volatility of biodiesel

KINEMATICS AND REACTION CONSTANT EVALUATION

Overall reaction:

$$TG(A) + 3M \rightarrow 3ME + GL$$

Overall reaction rate:

$$\frac{dX}{dt} = K(1 - X)^n;$$

Considering a 1st order reaction:

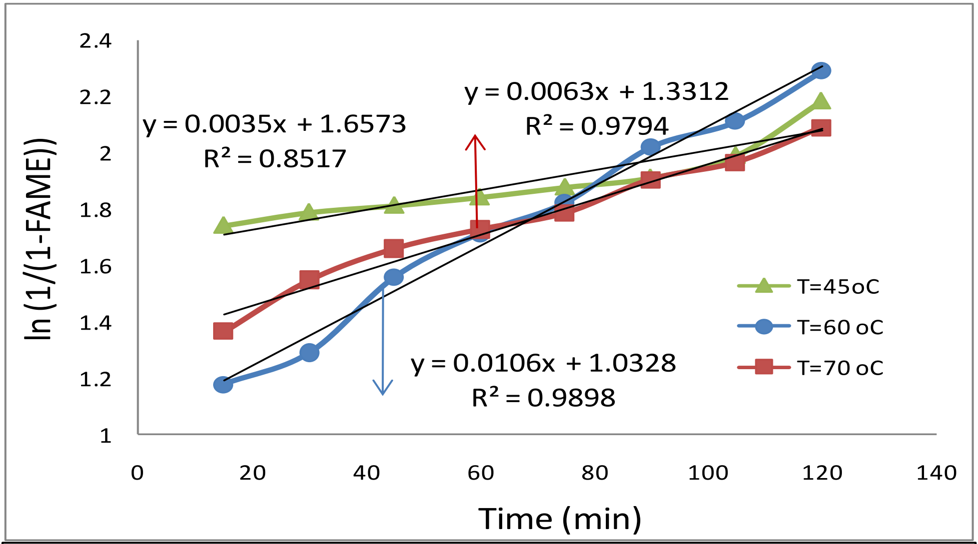
$$\ln\frac{1}{(1-x)} = Kt$$

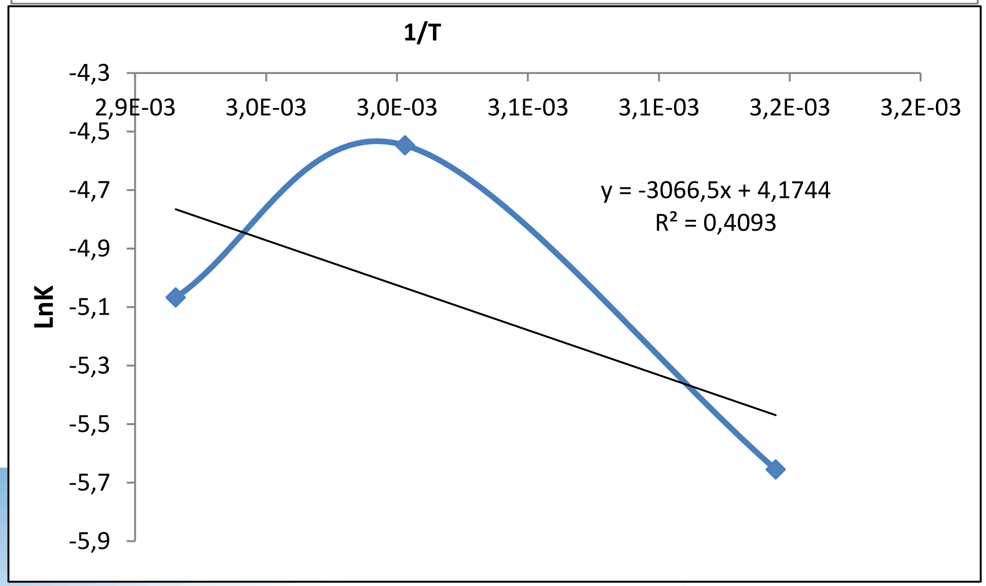
Arrhenius Equation

$$K = A\,e^{(-E/RT)}$$

The activation energy (E) at T= 45, 60, 70°C = **25,496 J/mol** and pre-exponent factor (A) = **4.1744**

A and *E* can be used in high Fidelity simulation





KINEMATICS AND REACTION CONSTANT EVALUATION

$$TG + A \underset{K2}{\overset{K1}{\longleftrightarrow}} E + DG$$

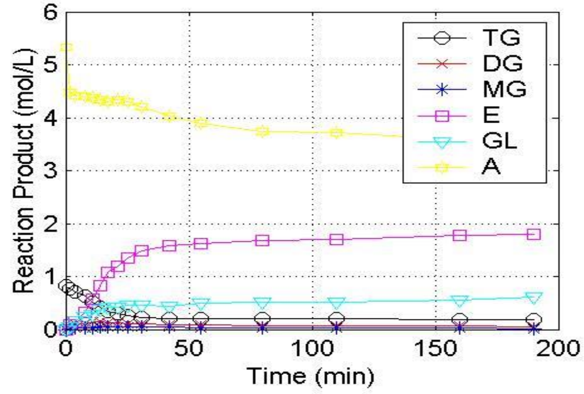
$$DG + A \underset{K4}{\overset{K3}{\longleftrightarrow}} E + MG$$

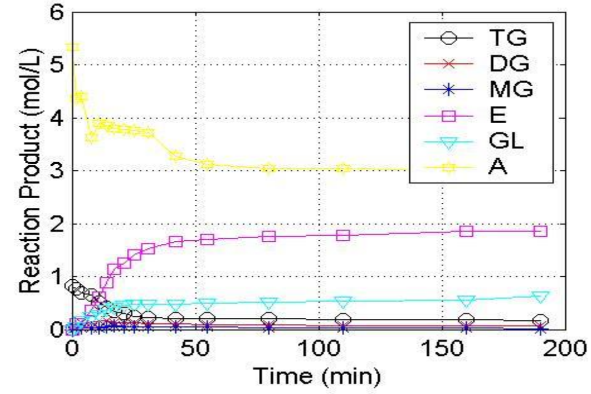
$$MG + A \underset{K6}{\overset{K5}{\longleftrightarrow}} E + GL$$

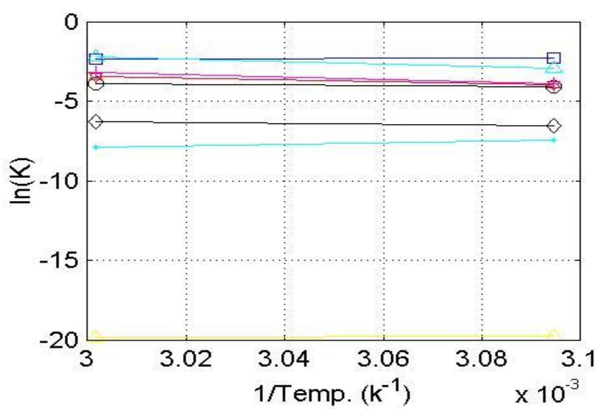
$$TG + 3A \underset{K8}{\overset{K7}{\longleftrightarrow}} 3E + GL$$

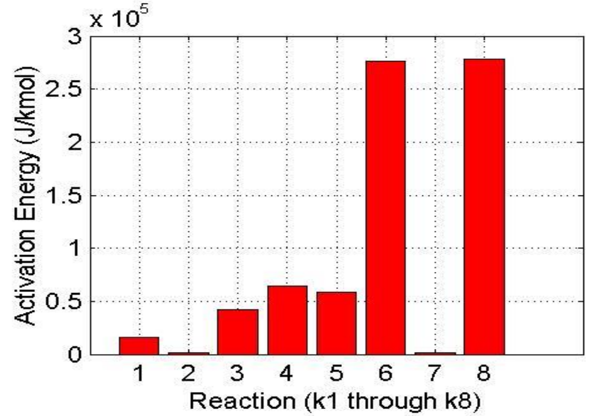
$$Ax = b \qquad x = A^{-1}b$$

$$K = Ae^{-E/RT} \qquad \ln K = \ln A - \frac{E}{R}\frac{1}{T}$$





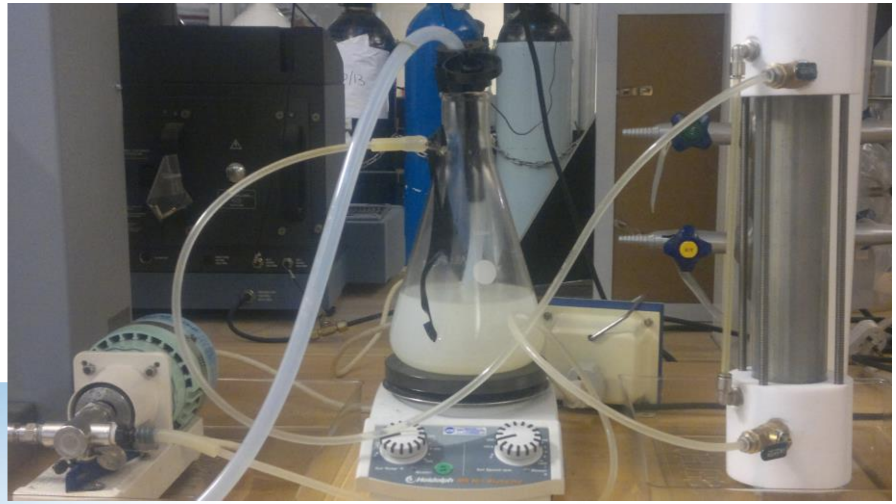




Reaction rate constant	K1	K2	K3	K4	K5	K6	K7	K8
WCO at 50^{o}C (this work)	0.0169	0.0994	0.0194	0.0531	0.0205	0.0015	2.5E-9	0.00056
WCO at 60^{o}C (this work)	0.0202	0.0975	0.0314	0.1106	0.0400	0.0018	2.5E-9	0.00037
Noureddini and Zhu [2]	0.049	0.102	0.218	1.280	0.239	0.007	7.84E-5	1.5E-5
Activation Energy kJ/kmol	E1	E2	E3	E4	E5	E6	E7	E8
WCO at 50-60 ^{o}C (this work)	0.1579	0.0172	0.4218	0.6438	0.5865	2.7648	0.01208	0.78100
Noureddini and Zhu [2]	0.0632	0.0477	0.0955	0.0704	0.0308	0.0461	-	-

HOMOGENEOUS BASE TRANSESTERIFICATION VIA CONTINUOUS PROCESS

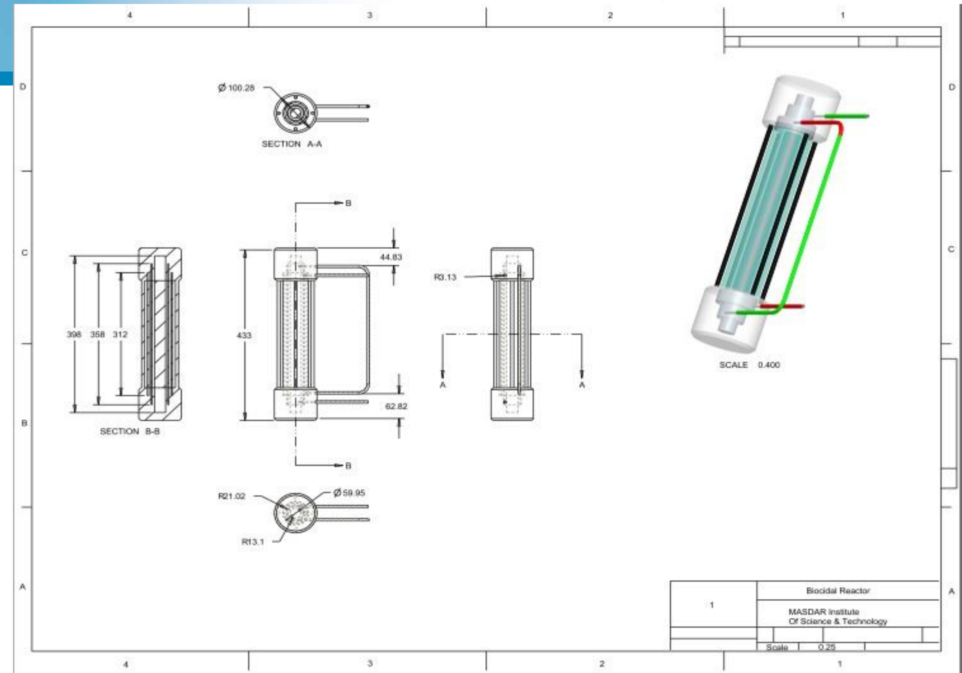
- Reactant is continuously pumped into the reactor
- To enhance the reaction:
  - Configuration must allow an increase in surface area per unit volume, efficient entrainments and mixing to enhance mass transfer, and component solubility at low pumping power.
  - Small flow mass →transfer limited two phase flow.
  - High flow rate → shorter residence time.

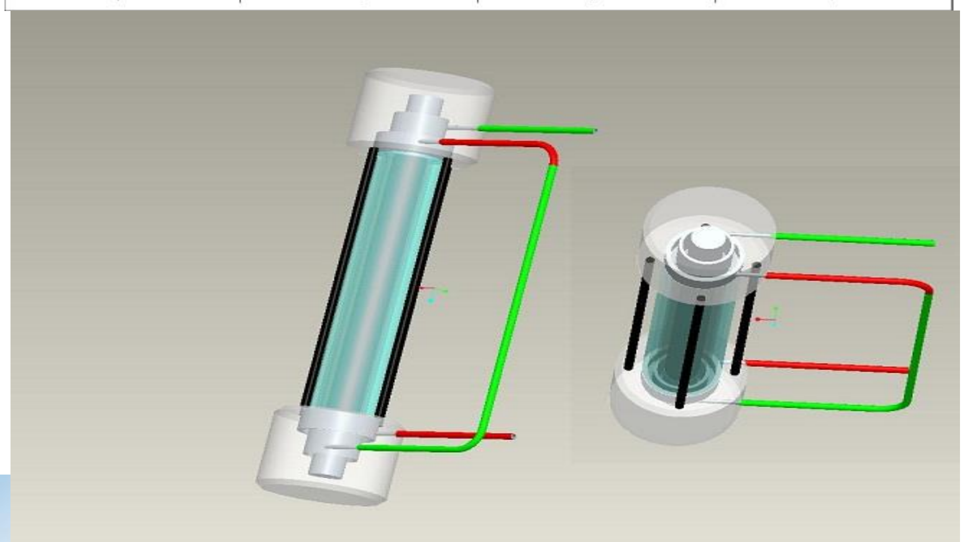


HOMOGENEOUS BASE TRANSESTERIFICATION VIA CONTINUOUS PROCESS

Reactor configuration

- 2 coincided separated chambers.
- Low pressure drop, ease of temperature control through and nearly isothermal reaction condition
- One peristaltic pump (pumps the fluid from the primary reservoir into the yield reservoir).
- Reactants are introduced circumferentially to increase flow residence time while following as a swirling trajectory
- Extraction of the product could be done in two stages → measure the efficiency of each loop and observing the conversion of the mixture to biodiesel:





HOMOGENEOUS BASE TRANSESTERIFICATION VIA CONTINUOUS PROCESS

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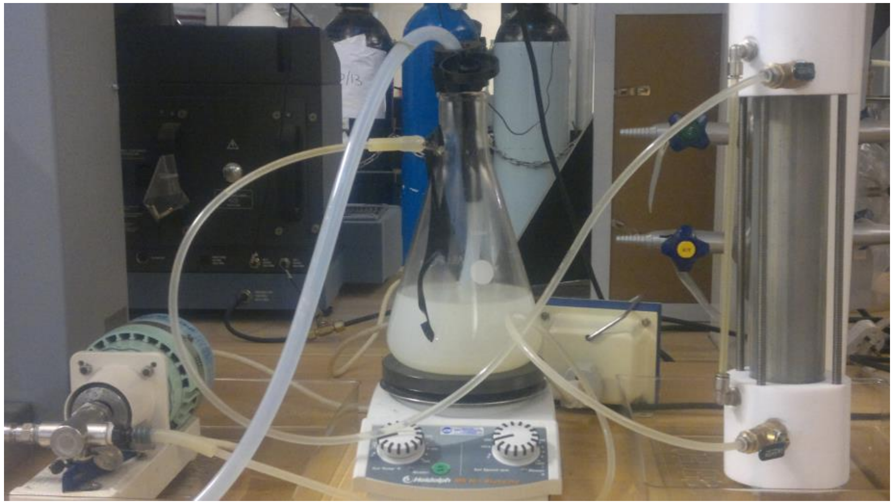
1. **Titration**
2. **Experiments Processing**

Exp.	Alcohol	Molar alcohol:oil	Catalyst	Catalyst conc. (%)	Time (hours)	Flow rate (ml/min)
Exp.1	Methanol	12:01	NaOH	0.5	2	100
Exp.2	Methanol	12:01	NaOH	0.5	2	300
Exp.3	Methanol	6:01	NaOH	0.5	2	100



3. Yield after experiments

Exp.	Residence time (min)	Yield %	Yield % (Batch)
Exp.1	14	94.85	90
Exp.2	10	86	90
Exp.3	14	91.87	64.5

- Alcohol to oil molar ratio
- Flow rate
- Continuous vs. batch at 6:1 molar ratio:
  - Advantage of efficient mixing of the flow

HOMOGENEOUS BASE TRANSESTERIFICATION VIA CONTINUOUS PROCESS

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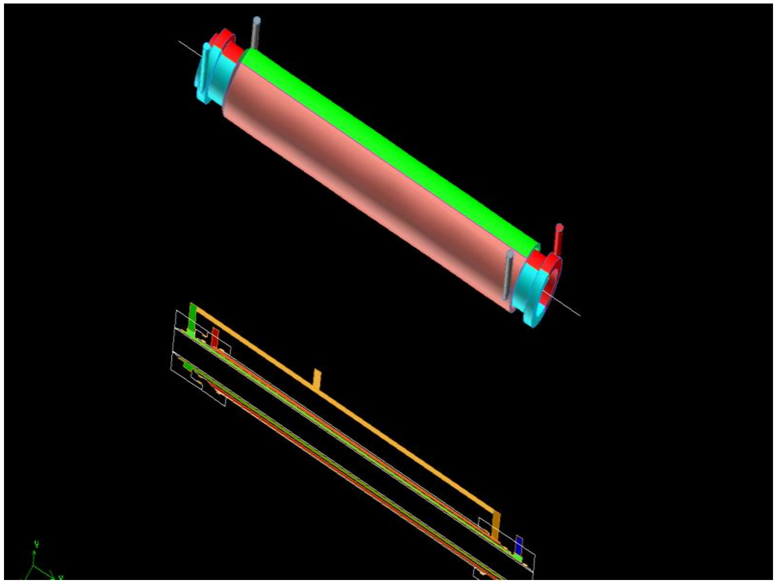
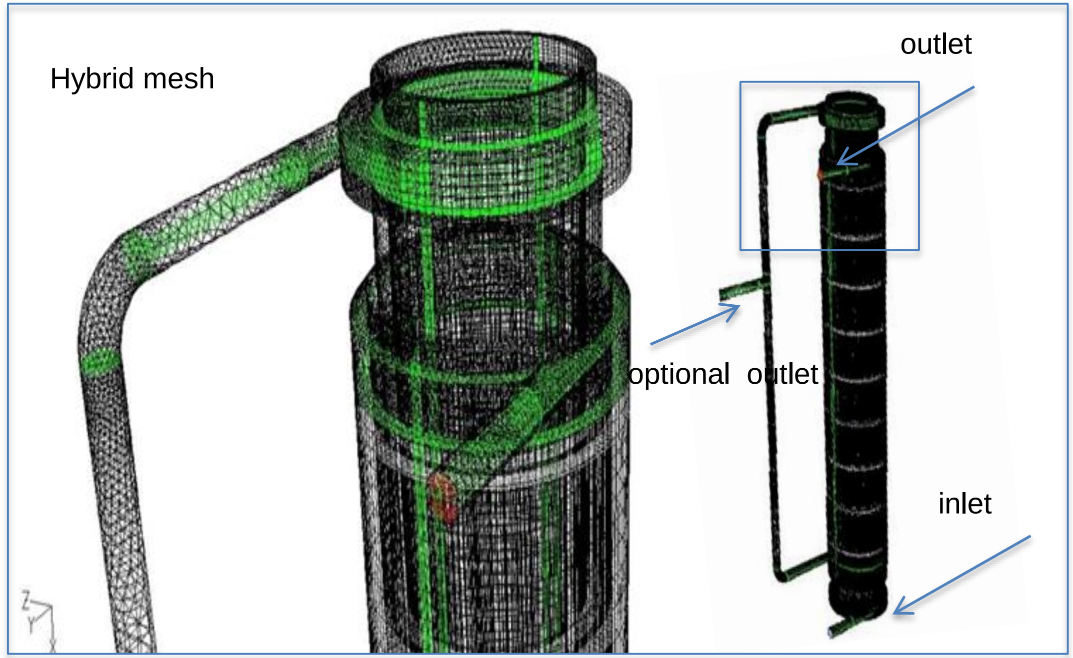
Properties of biodiesel produced from waste cooking oil (WCO) oil at 60 °C and 100 ml/min, Diesel and Biodiesel Requirement

Tests	Unit	Result	Biodiesel Requirement	Petro-diesel Requirement
Acid Number, Total	mg KOH/g	0.25	0.8 max	0.22
Cetane Number		63.3	48–65	40–55
Corrosion, copper (3 HR @ 100°C)		1	3 max	1
Density at 15^{0}C	kg/m^3	879.4	880	850
Flash Point	°C	175	130-170	88
Cloud Point	°C	+13.0	-3 –15	-35 – 5
Pour Point	°C	+12.0	-5 –10	-35 – -15
CFPP	°C	+10		
Viscosity @40^{o}C	CST	4.962	4.0–6.0	1.3–4.1
Lubricity (HFRR)	Micron	280	320	520

NUMERICAL SIMULATION OF TRANSESTERIFICATION OF WASTE COOKING OIL IN TABULAR REACTOR

A fine hybrid hexagonal and pyramid mesh is generated comprised of 281,382 cells & 729,741 faces for the two chambers and connecting tubing





Summary of species properties and MW

Species	Chemical formula	Molecular weight	Viscosity (kg/m.s)	Cp (J/kg.°C)	Density Kg/m^3
Methanol	CH_4O	32	3.96e-4	1.470e3	791.8
Waste oil	$C_{54}H_{104}O_6$	849	1.61e-2	2.2e3	883.3
Biodiesel	$C_{18}H_{36}O_2$	284	1.12e-3	1.187e3	870
Glycerol	$C_3H_8O_3$	92	1.412e0	0238.6	1261

NUMERICAL SIMULATION OF TRANSESTERIFICATION OF WASTE COOKING OIL IN TABULAR REACTOR

Mathematical System:

1) Continuity, Momentum, Energy, TKE (k), TDR (e):

$$\frac{\partial}{\partial t}(\phi) + \frac{\partial}{\partial x_i}(u_i\phi) = -\frac{\partial}{\partial x_i}\left(\Gamma_\phi \frac{\partial \phi}{\partial x_i}\right) + S_\phi$$

Time rate *advective* *diffusion* *source*

2) Transportation equation for m_i species:

$$\frac{\partial}{\partial t}(\rho m_i) + \frac{\partial}{\partial x_i}(\rho u_i m_i) = \frac{\partial}{\partial x_i}(\rho D_{i,m} + \mu_t / Sc_t)\frac{\partial m_i}{\partial x_i} + R_i + S_i$$

3) Reaction kinetics:

$$\sum_{i=1}^{N} v'_{i,r} S_i \underset{k_{b,r}}{\overset{k_{f,r}}{\Leftrightarrow}} \sum_{i=1}^{N} v''_{i,r} S_i; \quad R_{i,r} = M_{i,r}(v''_{i,r} - v'_{i,r})\left(k \prod_{j=1}^{N} C_{j,r}^{\eta^*_{,rj}}\right); \quad k = Ae^{(-E/RT)}$$

NUMERICAL SIMULATION OF TRANSESTERIFICATION OF WASTE COOKING OIL IN TABULAR REACTOR

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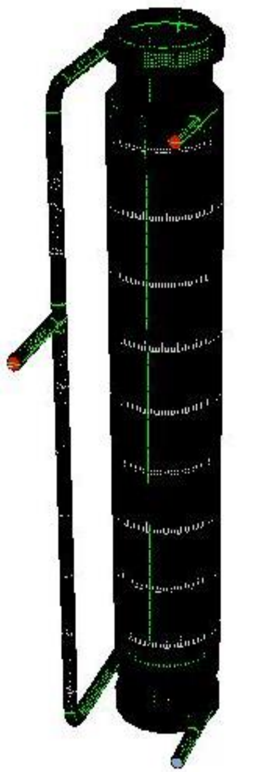
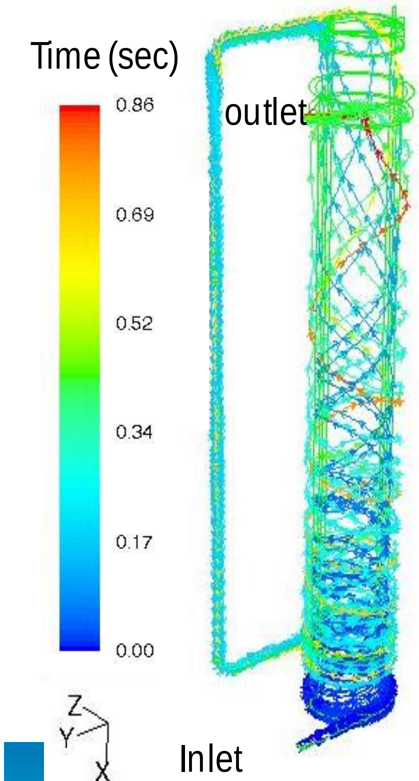
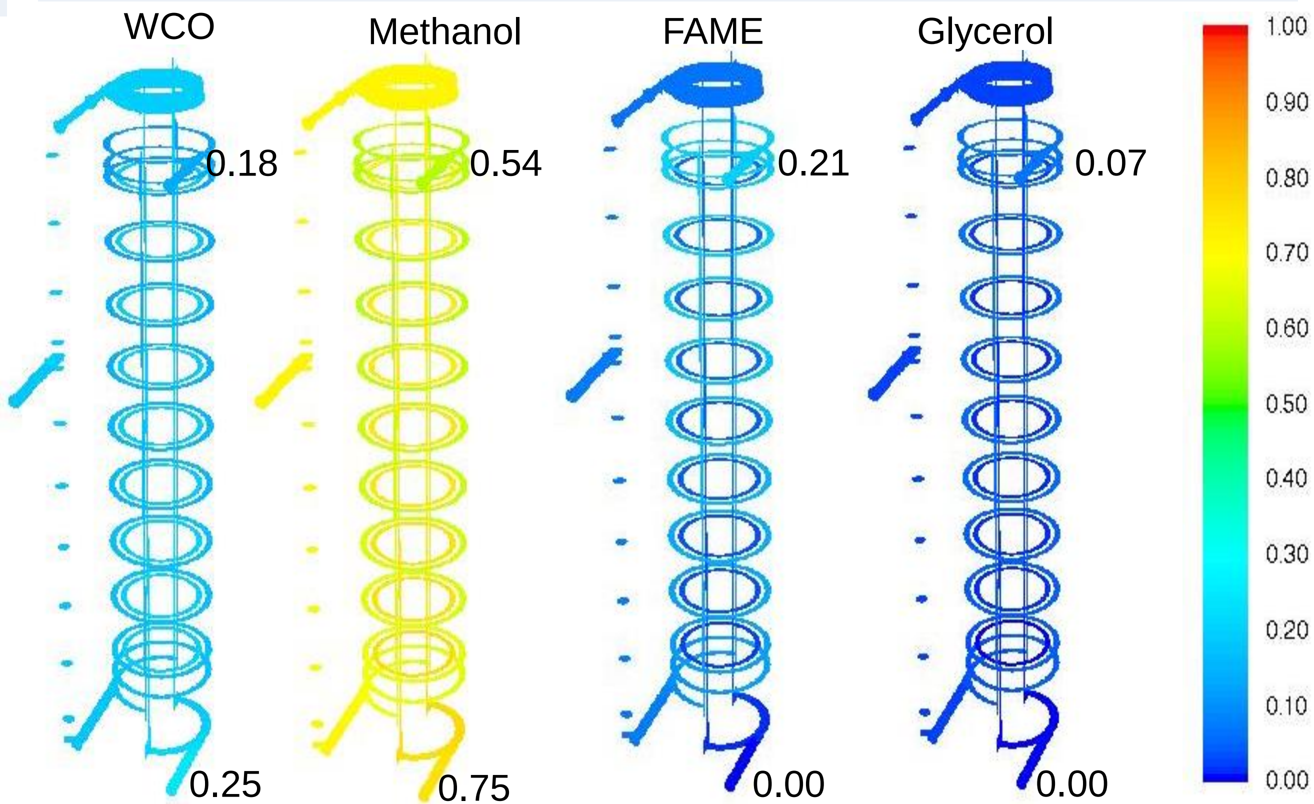
Mesh



Cold flow:
Flow trajectory colored by the resident time

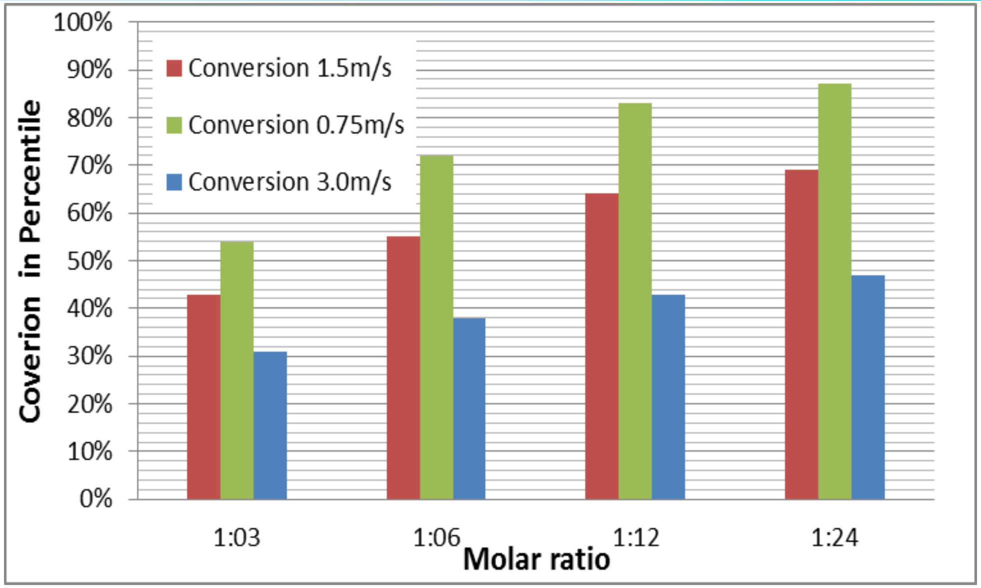


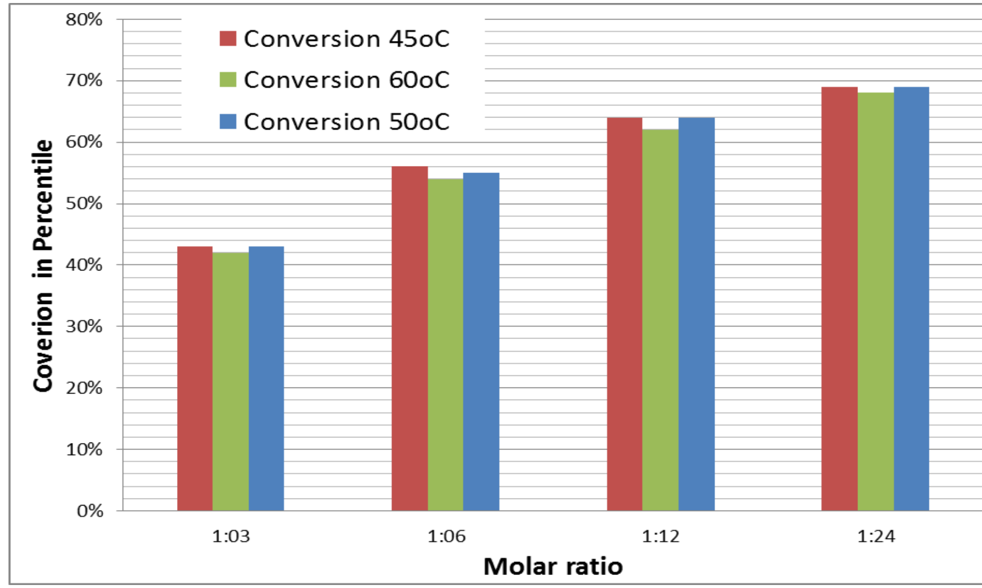
Reacting flow:
Molar fraction of species across the reactor at low mass flow conditions within the laminar regime (Re=1, based on the smallest tube diameter of 1cm)



X = 28%

NUMERICAL SIMULATION OF TRANSESTERIFICATION OF WASTE COOKING OIL IN TABULAR REACTOR





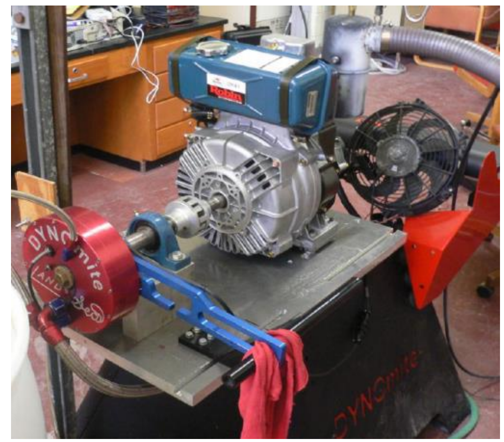
COMBUSTION AND EMISSIONS CHARACTERISTICS OF DIESEL AND BIODIESEL FUEL BLENDS IN SINGLE CYLINDER DIESEL ENGINE

Comparison of pressure and emissions from the diesel engine using bio-diesel fuel blends (B05, B10, and B20) and conventional petroleum diesel fuel.

Test engine 1:

Engine Model	G. CUSSONS SERIAL NO. P8160/132
Engine Type	4 stroke
Combustion System	Direct Injection
No. of Cylinders	Single
Cooling System	Air cooled
Bore x Stroke	76.2 x 111.1mm
Max Speed	2000 rpm
Max. Torque	7.5 N.m

Test engine 2: Eight horse power diesel engine.



Dynamometer: Measuring Torque and RPM, giving the engine HP by:

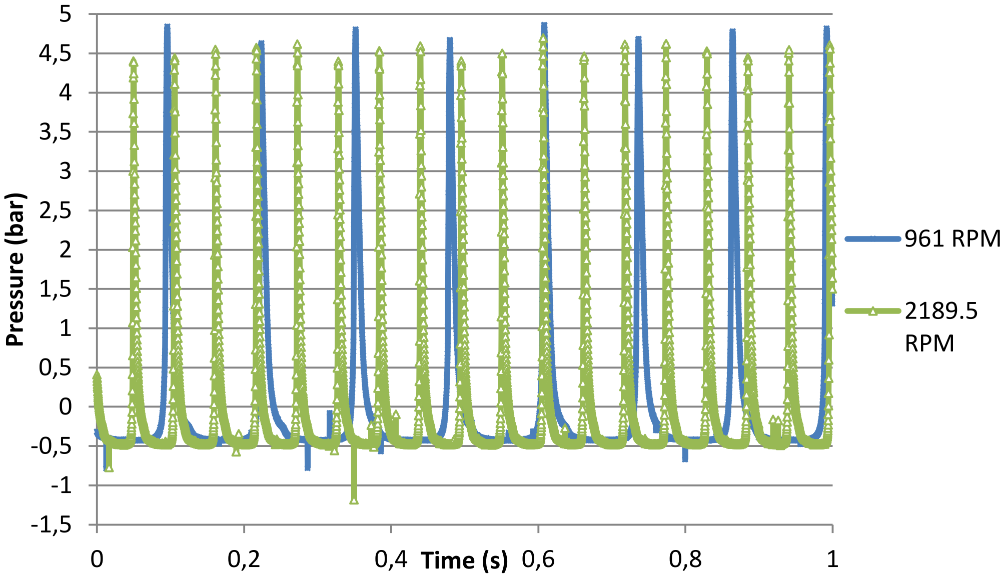
Horsepower = (RPM * Torque) / 5252

Gas analyzer: Measuring conc. of O_2, CO, CO_2, HC, and NOx

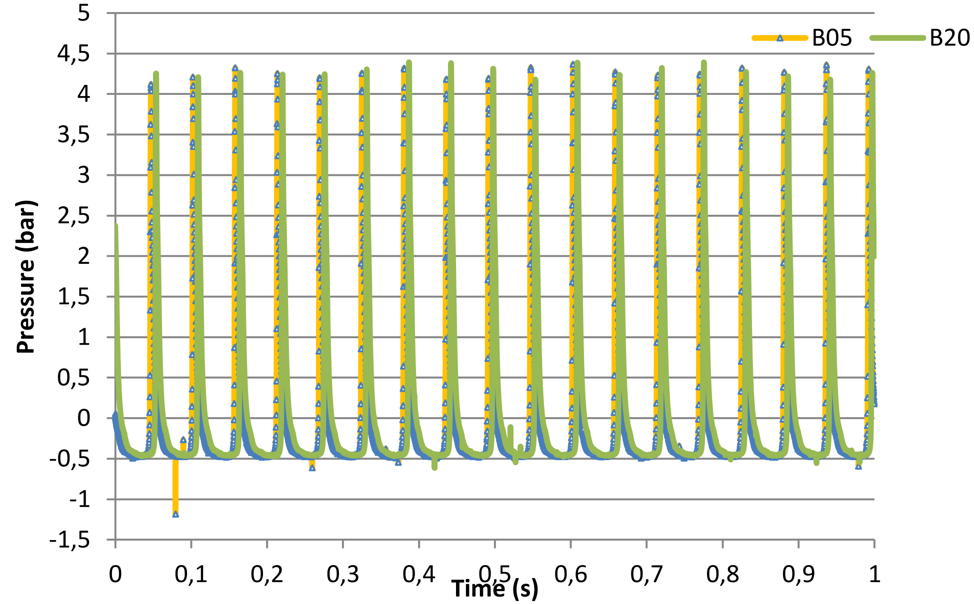
Engine test Procedure

- Run the engine for 2 minutes to allow the engine to clear any residue from previous tests with different fuel blends, and warm up the engine and catalyst.
- After the 2 minutes, warm up the engine at low RPM for 5 minutes
- Increase the engine speed to medium RPM and run the engine for 5 minutes
- Finally set the engine to high RPM and run it for 5 minutes

In-Cylinder pressure of Petroleum Diesel and biodiesel blends Fuels



Engine cylinder pressure, versus time (seconds) - Petroleum Diesel fuel at low and high RPM.



Engine cylinder pressure, versus time (seconds) - Biodiesel Fuel Blends at high RPM

Emission characteristics of Petroleum Diesel

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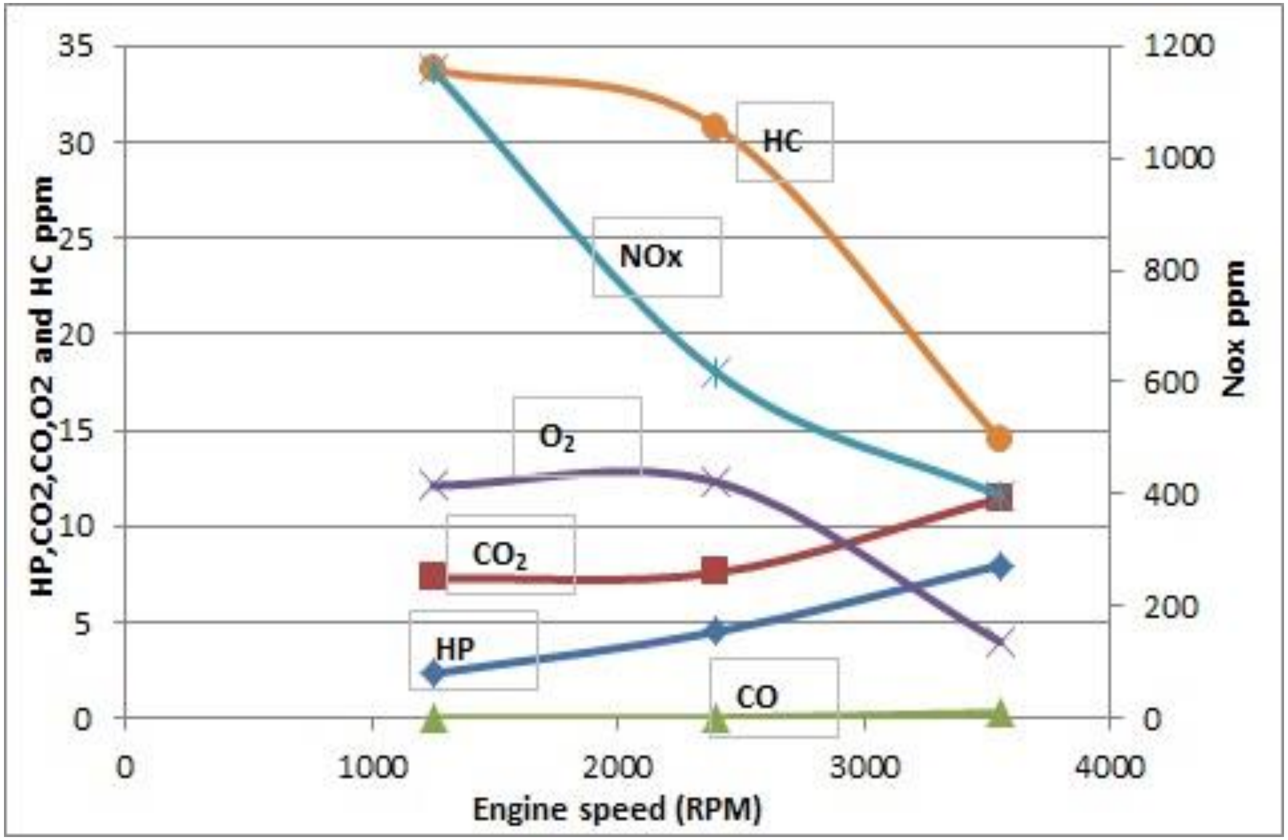

Engine emissions at different RPM – Petroleum Diesel fuel

Emission characteristics of Biodiesel Fuel Blends

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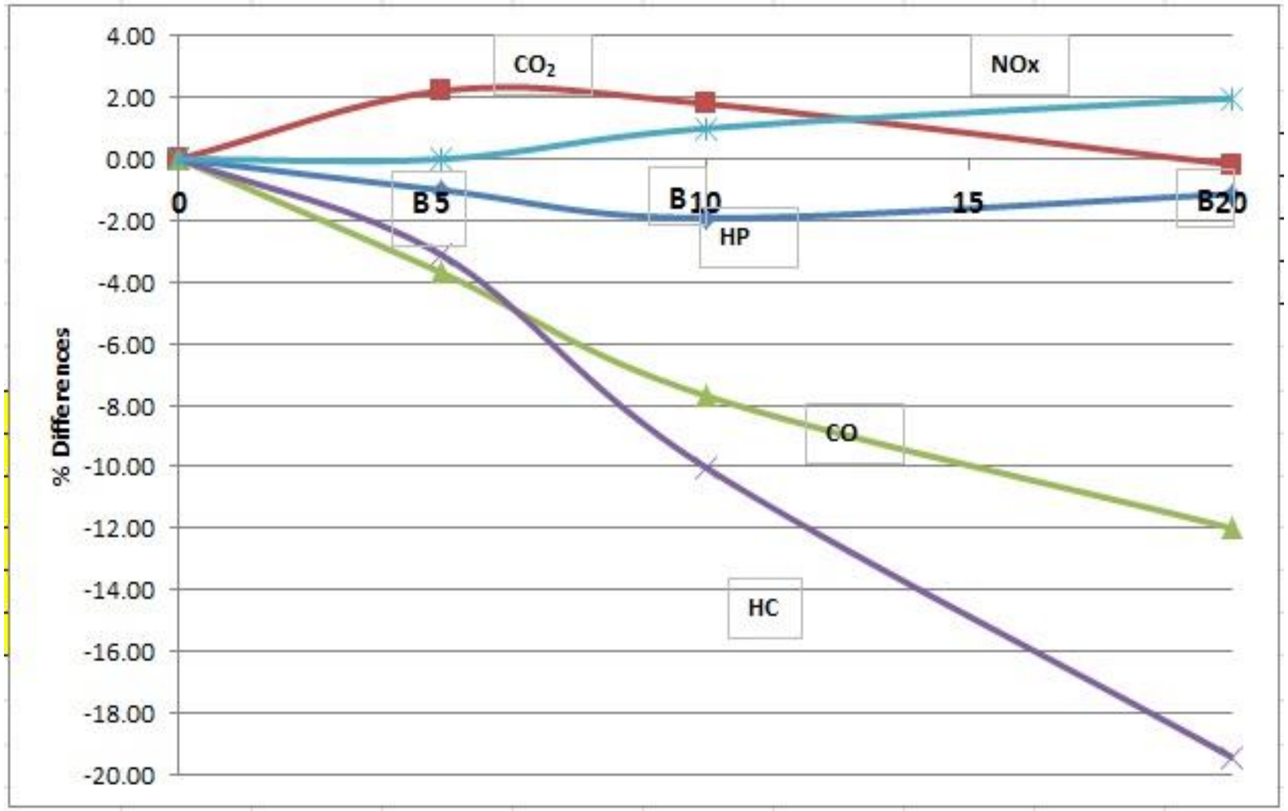
Results:



Overall percentage differences of biodiesel fuel blends with respect to petroleum Diesel

- **HC emissions** for the B20 decreases by about 20% compared to PD.
- The **CO emissions** decrease by about 12 % for the B20.
- Small decrease (< 2%) in **engine power** (HP) for B20.
- **CO_2** and **NOx** emissions increase slightly for B20.

CONCLUSION

- Biodiesel was produced by homogeneous alkaline transesterification
- The highest yield was achieved by using the lower catalyst concentration of 0.5% NaOH
- All fuel properties fell within the requirements of American standard for biodiesel fuel
- Optimal process was found to follow 1^{st} order reaction rate with a rate constant of 0.01 min^{-1} and the activation energy was found to be 25,496 J/mol (opportunity for High Fidelity analysis and innovative reactor development)
- A new reactor configuration is proposed showing that increasing the flow rate, decrease the yield from 94.6% to 86% and gives better results especially with the 6:1 molar ratio
- The outcomes of the engine testing showed that the engine is stable since the cycles are almost identical.
- The hydrocarbons HC and CO emissions decreased by increasing the amount of biodiesel blended with Petroleum Diesel. The HC and CO emissions decreased respectively by 20 % and 12 % for the B20 compared to the Petroleum Diesel.
- NO_x emissions increased by 2% and the change of the engine power was negligible (<2%).

Thank You

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- R. Abd Rabu, I. Janajreh, D. Honnery, Transesterification of waste cooking oil: Process optimization and conversion rate evaluation, Energy Conversion and Management, Volume 65, January 2013, Pages 764-769, ISSN 0196-8904, http://dx.doi.org/10.1016/j.enconman.2012.02.031.
- Janajreh, I. and Al Shrah, M. (2013). "Numerical Simulation of Multiple Step Transesterification of Waste Oil in Tubular Reactor." J. Infrastruct. Syst., 10.1061/(ASCE)IS.1943-555X.0000183 (Aug. 3, 2013).
- R. Abd Rabu, and I. Janajreh, D. Honnery, ‘’Transesterification of Waste Cooking Oil: Process optimization and kinetic evaluation ’’ ISAF 2011, Verona-Italy, October 2011
- I. Janajreh, M. Al Shrah, Development of Continuous and Modular Transesterification Reactor For Efficient Bio diesel Production from Waste Oil, 10th Global Conference on Sustainable Manufacturing (GCSM2012), Istanbul, Turkey, Oct 31st –Nov 2nd 2012.
- Patents: I.Janajreh, R.Abd Rabu. Dual Chamber Tubular Reactor for Continuous Transesterification of Waste Cooking Oil