Enhancement of Sapindus Trifoliatus Biodiesel Production and Performance using Mg-doped CaO Nanocatalyst

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Research Article

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Abstract

The use of biodiesel can reduce dependence on diesel and stabilize the economy when using internal combustion engines. CI engine's performance with biodiesel is substantially low but could be improved by emulsifying nano-additives with biodiesel. Magnesium-doped Calcium Oxide, a novel nanocatalyst is emulsified in its nano form with the *Sapindus Trifoliatus* biodiesel (STBD) at B25 blend (STBD25+Mg-CaO 30ppm) and tested in the CI engine. The performance results obtained are compared to the baseline values obtained using diesel, *Sapindus Trifoliatus* biodiesel (STBD25), and *Sapindus Trifoliatus* biodiesel blended with Cao nano additives (STBD25+30ppm CaO) in the CI engine. . A maximum biodiesel yield of 91.75% was achieved at 58°C, 73 min, a catalyst concentration of 4% (%w / %w) and a methanol: oil molar ratio of 15:1. From the comparison, it is revealed that (i) In-cylinder pressure found to be increased by 3.22%, 6.24% and 9.02%, (ii) HRR increases by 1.68%, 16.69% and 32.5%, (iii) BTE is found to be increased by 4.56%, 8.23% and 11.79%, (iv) UHC decreases by 21.12%, 6.06% and 11.43%, (v) CO decreases by 0.04%, 0.01% and 0.01%, (vi) Smoke decreases by 54.52%, 9.34% and 19.58%, compared with diesel, STBD25+30ppm CaO and STBD25. NOx released while using STBD25+Mg doped CaO in CI engine was observed to decrease compared with STBD25 and STBD25+CaO (by 10.72 % and 18.64 %) and increase compared with diesel (by 8.64%). Whereas an insignificant drop in NOx was observed while using STBD25+Mg doped CaO as fuel compared with STBD25+CaO and STBD25 in spite of a significant increase in HRR and BTE which might be due to the capture of excess oxygen by Mg during the combustion diffusion phase.

1. Introduction

In the current scenario, mobility is solely dependent on fossil fuel which is a non-renewable source of energy (Turkdogan 2021). The booming global energy demand is overexploiting this fuel and hence these energy reserves are depleting (Kumar and Rehman 2016). To meet growing energy demands and protect the environment from other harmful pollutants, biodiesel is one of the best alternative fuels that can be used in conventional engines, with or without minor modifications (Bharathiraja et al. 2014). Due to the increase in demand for fossil fuels like Gasoline and Diesel, the usage of other alternative fuels (Farooq et al. 2020). The various factors like fuel distribution, energy storage, emissions, performance, and much more are needed to be considered when into switching to a better alternative fuel (Duarte Souza Alvarenga Santos et al. 2021). It is also to be noted that it has low emission of toxic gases like carbon monoxide (CO), Sulphur dioxide (SO_2). This is possible when the sulfur content in the fuel is less (Chukwuezie et al. 2014) and is both economically and environmentally feasible. The best solution for this is using Biofuel as it helps in tackling the emission of greenhouse gases and also requires little to no change in the design of the transmission and combustion system (Mesri Gundoshmian et al. 2021).

The adaptation towards biofuel has increased in the last few years due to the rise in demand and also by the adoption of various government reforms by the top developed countries like the US, Germany and other such countries (Ogunkunle and Ahmed 2019). Biodiesel can be produced from algae where it is fermented and dewatered to convert it into bioethanol (Prabakaran et al. 2021). Another way is the extraction of oil from seeds like Jatropha, where the extracted oil is transesterified for usage (Chen et al. 2012). Another source is the Sapiens seeds, also known as Soapnut. It is commonly referred to as Soapberry or Washnut in India. It has a high content of 23% oil which contains 92% triglycerides. In addition, the oil content of the core is about 42.7% by weight (Chen et al. 2013). The most important fatty acids in soapnut oil are oleic acid and eicosanoid acid. The high monosaturated fatty acid content of soapnut oil is an important feature compared to the normal fatty acid profile of vegetable oils. It also has better oxidation stability (Misra and Murthy 2011). The oils can't be used directly, so it is blended with diesel with blending ratios of 1:10 or 2:10 which is found to provide better viscosity (Rizwanul Fattah et al. 2013). A possible way is the use of pyrolysis where the methyl ester compounds (Chen et al. 2018) like animal fat, and vegetable oils are converted to another substance by the application of heat and with or without the use of a catalyst. Another way is by the use of hybrid fuels, where micro-emulsions are used to make colloidal equilibrium. 1-butanol, methanol, and ethanol are the solvents that have been investigated, and microemulsions containing butanol, hexanol, and octanol can meet the maximum viscosity limits of diesel engines (Raut et al. 2018).

The diesel engine is the best fit as its performance for power generation is much higher. It works well even at low engine loads (Uyumaz 2018). The emissions of the diesel engine would be substantially reduced by fuel injection, turbocharging, supercharging and also by the use of a perfect blend of biodiesel (Mustayen et al. 2022). Nanoparticles emulsified with biodiesel shorten ignition delay, accelerate the early onset of combustion, reduce HRR, and lowers In-cylinder peak pressure at full load (Prabhu and Venkata Ramanan 2018). The addition of nanoparticles improved the BTE and reduced the BSFC (Kumar and Raheman 2021) by 6.58% and 7.38% respectively. As a result of improved combustion efficiency, adding fuel-based additives to PBD improved emissions of Hydrocarbon, Carbon Monoxide, Oxides of Nitrogen and smoke opacity (Venu and Appavu 2020). Magnesium-doped Calcium Oxide was obtained by the calcination process of eggshells and then treated with a 1M solution of magnesium water. As a result, a precipitate containing CaO-Mg $(OH)_2$ was obtained, which was further heated at 10° C./min to 450–500° C. for 3 hours to remove Mg $(OH)_2$ in the catalyst structure, calcined in MgO (Foroutan et al. 2020).

In this research paper, *Sapindus Trifoliatus* oil was extracted from *Sapindus Trifoliatus* fruit by the combined mechanical and chemical solvent method (Ali and Watson 2014). The heterogeneous novel catalyst was prepared and used for the transesterification process (Mares et al. 2021). A new type of catalyst, magnesium-doped calcium oxide, is emulsified in nano-form with *Sapindus Trifoliatus* biodiesel (STBD) in an STBD25 mixture (STBD25 + 30ppm Mg-CaO) and tested in a CI engine. Experimental results using diesel, biodiesel (STBD25), biodiesel emulsified with CaO nano additives (STBD25 + 30 ppm CaO), and biodiesel emulsified with Mg-CaO nano additives (STBD25 + Mg-doped CaO) are compared to baseline measurements obtained by with a CI engine.

1.1 The novelty of this research Article

Analysis of various research papers on biodiesel and nano additives revealed no behavioral studies have been conducted on an unmodified CI engine performance using CaO and Mg-doped CaO nanoparticles emulsified with *Sapindus trifoliatus* biodiesel. Starting with this research, the experimental study was carried out using raw diesel, *Sapindus trifoliatus* biodiesel and CaO nano additives blended with *Sapindus trifoliatus* biodiesel and Mg-doped CaO nano additives blended with *Sapindus trifoliatus* biodiesel. The working procedure of the current experiment is shown in Fig. 1.

2. Materials And Methodology

2.1 Specimen collection and preparation

150 kg of *Sapindus trifoliatus* fruits were bought from an Ayurvedic shop in Sowcarpet, Chennai, Tamil Nadu, India. *Sapindus* fruits were air-dried for 30–40 days to remove moisture. Gypsum plaster was collected at a construction site in Chennai, Tamil Nadu, India. Pure chemicals such as H_2O_2, magnesium nitrate, methanol and ammonia are sourced from Chem Laboratory Pvt. Ltd., Mumbai for biodiesel production and catalyst synthesis. To avoid further purification processes, 99% pure chemicals were used, and deionized double-distilled water was also used in this study.

2.2 Extraction of Oil

The air-dried *Sapindus trifoliatus* fruits are pealed to get the nuts and then the nuts are soaked in water for 2–3 weeks for softening process (Chen et al. 2019). Further *Sapindus trifoliatus* nuts are crushed to get the kernels of 69 kg. The workflow carried out in the oil extraction is shown in Fig. 2.

The moisture content of the *Sapindus trifoliatus* kernels was observed to be 31–34%, hence *Sapindus trifoliatus* kernels are air dried for 5 to 10 days and the moisture content got reduced to 8–10%. The *Sapindus trifoliatus* oil was extracted from a vendor in Tambaram, Chennai, Tamilnadu. The yield of *Sapindus trifoliatus* oil was 24.3kg and the percentage of oil content in the kernel varied from 50–55% (w/w) (Chakraborty and Baruah 2013). The thermophysical properties of *Sapindus trifoliatus* oil such as density, flash point, kinematic viscosity, fire point, pour point, calorific value, iodine number, saponification number content, cloud point (Amin et al. 2016), etc. are shown in Table 1. It was measured by a standard test method.

Table 1
The thermodynamic properties of *Sapindus trifoliatus* oil

Fuel Property	Units	*Sapindus trifoliatus* Oil	Diesel	ASTM standard
Density	kg/m^3	912	840	ASTM D1298 (20 ºC)
Kinematic viscosity	mm^2/s	45.4	2.84	ASTM D445 (40 ºC)
Lower calorific value	kJ/kg	38,542	42,700	ASTM D240
Flashpoint	ºC	232	68	ASTM D93
Fire point	ºC	240	77	ASTM D93
Pour point	ºC	6.9	3.2	ASTM D 2500
Saponification value	mg/fat	196.54	-	IS 548:1964
Iodine value	g/100g	77.42	-	IS 548:1964
Cloud point	ºC	15.3	6.4	ASTM D 2500

3. Catalyst Synthesis And Characterization

3.1 Catalyst synthesis

300g of gypsum plaster was heated at 135°C for one hour, which results in a hemihydrate with three-quarters of the water removed as shown in Eq. 1. Plaster of Paris is another name for Gypsum hemihydrate.

$$\mathrm{CaSO_4.2H_2O 135℃ \rightarrow CaSO_4.\tfrac{1}{2}H_2O\,(hemihydrate)}\ (1)$$

$$\mathrm{CaSO_4.\tfrac{1}{2}H_2O\,(hemihydrate)\,600℃ \rightarrow CaSO_4\,(anhydrite)}\ (2)$$

The dissolved impurities in the plaster of Paris (PoP) were removed and purified using H_2O_2 and hot water as shown in Fig. 3. PoP and 30% H_2O_2 were mixed at 45 ºC for 3.5 hrs and washed with hot water 4 times. To remove the volatile materials in PoP, the PoP was dried at 110 ºC for 16 hrs and further calcinated at 600 ºC to 800 ºC (Naveenkumar and Baskar 2019).

$$\mathbf{CaSO_4\,(anhydrite)}\,800\mathbf{℃} \rightarrow \mathbf{CaO} + \mathbf{SO_3}\ (3)$$

Solution-A was prepared using 0.55 g CaO mixed with 50 ml distilled water. For solution-B, 7.2 g of magnesium nitrate was dissolved in 50 ml of distilled water. A-solution and B-solution were mixed in an appropriate ratio, 8% ammonia was mixed, and the solution mixtures were stirred at regular intervals for 2 hours. 0.4 M Na_2CO_3 was added to the mixture for precipitation and for the aviation process, the mixture was precipitated and dried for 3 hrs at 80 ºC, the dry powder was then calcined at 900 ºC as shown in Fig. 4.

3.2 Characterisation of Catalyst

SEM, FTIR and EDAX characterizations were used to study the structural and morphological characteristics of the synthesized Mg-doped CaO and nanocatalyst(Muninathan et al. 2022) from Fig. 5, Fig. 6 and Fig. 7. Various techniques were used to verify the size, morphology, and chemical properties of the synthesized catalysts.

Analysing functional groups of activated and functionalized samples by FTIR in organic, inorganic, and polymeric materials (Shylesh et al. 2007). High-quality spectral lines were obtained by recording spectra from 4000 to 500cm^{-1} in 4cm^{-1} resolution mode. A technique that uses X-ray diffraction (XRD) to analyze nanoparticle crystal structures in the range of 10–100 º2θ.

A surface topography analysis of the synthesized Mg-doped Cao catalysts was conducted using SEM.

3.3 Production of Biodiesel via Transesterification

The *Sapindus trifoliatus* oil was pre-treated at 90°C for 1 h to remove the moisture. For the transesterification process, the heterogeneous catalyst Mg-doped CaO is used. Appropriate conditions for the transesterification process were achieved by mixing methanol with synthesized heterogeneous Mg doped CaO catalyst at appropriate ratios. A mixture of methanol and Mg-doped CaO catalyst was mixed with *Sapindus trifoliatus* oil and the resulting mixture was stirred using a magnetic stirrer until the color turned black (Esipovich et al. 2018). The *Sapindus trifoliatus* biodiesel obtained after the transesterification process, at the top is removed after removing the precipitates such as glycerol and catalyst settled at the bottom of the separating funnel, and the prior is stored for further process. The separated biodiesel is heated to 65°C to get rid of extra methanol and washed with warm water to get rid of unreacted oil and impurities. Continuous cleaning may alter the pH, hence, stabilizing the same and removing the excess moisture content. The cured biodiesel is heated at 110°C for 10min. A maximum biodiesel yield of 91.75% was achieved at 58°C, 73 min, a catalyst concentration of 4% (%w / %w) and a methanol: oil molar ratio of 15:1 (Muninathan et al. 2022).

Extracted biofuel is not suitable to use directly (STBD100) in CI engines due to its high viscosity, high density and low calorific value (Celik et al. 2016). Hence, the biofuel is blended with diesel at concentrations of STBD25%+75%Diesel, STBD50%+50%Diesel, and STBD75%+25% Diesel and subjected to testing. STBD25 fuel property is closer to diesel as shown in Table 2 and the addition of 3% Tween 80 emulsifier improved solubility and stability.

Table 2
Thermodynamic Properties of blended fuel (STBD)

Fuel Property	Units	ASTM Standard	Diesel	STB25	STB50	STB75
Density	kg/m^3	ASTM D1298 (20 ºC)	840	853	866.94	884.78
Kinematic viscosity	mm^2/s	ASTM D445 (40 ºC)	2.84	4.5	4.67	5.83
Calorific value	kJ/kg	ASTM D240	42700	40638	39124	38976
Cetane Index	-	ASTM D613	43	48	50	51
Flashpoint	ºC	ASTM D93	59	71	75	77
Fire point	ºC	ASTM D93	68	80	82	85

3.3 Sample Preparation

Four samples were taken for experimental analysis of CI engine characteristics which are performance, combustion and emission. Sample A, raw diesel (ASTM standards) purchased from a local vendor, Chennai. Sample B, Sapindus trifoliatus biodiesel. Sample C, Sapindus trifoliatus biodiesel emulsified with 30 ppm CaO nanoparticle. Sample D, Sapindus trifoliatus biodiesel emulsified with 30 ppm Mg doped CaO nanoparticle. The nanoparticles are emulsified with biodiesel using a magnetic stirrer followed by ultrasonication for 45 min and 10 min respectively (Soudagar et al. 2021). The fuel properties of the four samples are listed in the Table 3 and comply with ASTM standards.

Table 3
The thermodynamic properties of the fuel emulsified with Mg-CaO Nano additives

Fuel Property	Units	Diesel	STB25	STB25 + CaO30	STB25 + MgCaO30
Density	kg/m^3	840	853	855.6	858.75
Kinematic viscosity	mm^2/s	2.84	4.5	4.65	4.71
Lower calorific value	kJ/kg	42,700	40,638	41,028	41203
Cetane Index	-	43	48	51	53
Flashpoint	ºC	59	71	75	77
Fire point	ºC	68	80	82	85

4. Experimental Setup And Procedure

In this experiment, an eddy-current dynamometer loaded with a four-stroke, single-cylinder variable compression ratio (VCR) diesel engine with electric starting has been used (Fig. 8). The injection pressure, injection timing and compression ratio measurements are interfaced to the computerised digital meter through various sensors with the help of a software called Enginesoft. This engine setup has an electric input of single phase, 230 +/- 10V AC and 50 Hz. Also, it requires a continuous clean and soft water supply @1000LPH, at 10 m head. The signals scanned during the process can be stored and presented in the form of graphs and tabular formats. Initially the engine is running to warm up about 20 minutes at a rated speed of 1500 rpm without any load using neat diesel fuel. The fuel blends are supplied to the engine after warming up through a separate tank (Venu and Madhavan 2016). The specifications of the engine and instruments used are shown in Table 4 and Table 5.

Table 4
The engine specifications

Specifications	Units	Type / Dimensions
Type	-	Kirloskar, water cooled, Single-Cylinder, 4 strokes, Diesel Engine
Bore X Stroke	$mm \times mm$	87.5×110
Compression Ratio	-	17.5 : 1
Rated Power	kW	3.5
Rated Speed	rpm	1500
Swept Volume	cc	661
Nozzle Diameter	mm	0.3
No. Nozzles	-	3
Cone Angle	Degree	120
Injecion Timing	Degree	23º before TDC
Piston	-	Hemispherical
IVO bTDC	Degree	4.5
IVC aBDC	Degree	35.5
EVO bBDC	Degree	35.5
EVC aTDC	Degree	4.5

Table 5
Device specifications and their accuracy

Device Specification	Units	Range	Accuracy	Uncertainties
Pressure Transducer	MPa	0–10	± 0.1	± 0.1
Crank angle encoder	Degree CA	0-720	0.2	± 0.2
Digital Tachometer	rpm	0-15000	± 10	± 0.1
Eddy Current Dynamometer	W	200–8000	15	± 0.3
Fuel Flow Meter	cc	1–30	± 0.1	± 1
EGT	ºC	0-900	± 1	± 0.15
Gas Analyser QRO-402				
CO	Vol%	0–10	± 0.02	± 0.2
HC	ppm	0-10000	± 20	± 0.2
NO_x	ppm	0-5000	± 10	± 0.2
CO_2	Vol%	0-19.99	± 0.03	± 0.15

5. Results And Discussion

The Mg-doped CaO and CaO nano additives were emulsified with *Sapindus Trifoliatus* biodiesel and investigated in the CI engine. The experiments were conducted using four different samples such as raw Diesel, STBD, STBD25 + 30 ppm CaO and STBD25 + 30ppm Mg doped CaO Nano additives. The engine performance, combustion and emission parameters have arrived at a constant speed of 1500rpm. Experiments were conducted with a bTDC injection timing of 23 degrees, 220 bar injection pressure and 18:1 compression ratio at different load conditions of 0%, 25%, 50%, 75% and 100% using a 4-stroke single-cylinder diesel engine. The engine is experimentally tested with *Sapindus Trifoliatus* biodiesel, with and without nano-additives, and the results are compared to conventional diesel fuel.

5.1 Effect of Mg-doped CaO Nano Additives on In-Cylinder Pressure

The development of in-cylinder pressure in an internal combustion engine depends only on the amount of fuel burned during the uncontrolled combustion (premixed combustion) stage (Ali et al. 2019). Cylinder pressure is an important parameter when analyzing the combustion characteristics of test fuels. Factors that affect cylinder pressure variation include viscosity, cetane number, ignition delay, and air/fuel mixture ratio (Imdadul et al. 2017; Emiroğlu and Şen 2018; Çeli̇k and Bayindirli 2020). Figure 9 shows changes in cylinder pressure with respect to the crank angle under full load conditions. From the graph, the in-cylinder pressure of STBD25 + 30ppm Mg-doped CaO increased by 3.22%, 6.24%, and 9.02% in percentage variation rate compared to diesel, STBD25-30ppm CaO, and STBD25. Diesel's low in-cylinder pressure is due to the shortened ignition delay time (Feng et al. 2020; Sahu et al. 2021), which made combustion uniform. Additionally, Table 2 shows the improved calorific value of diesel fuel. This helps to reduce fuel consumption, improve combustion efficiency, and shorten peak pressure (Qi et al. 2009; Saravanan et al. 2020). The addition of 30 ppm Mg-doped CaO nano-additive to STBD25 increased the peak pressure. This was attributed to the increased thermal conductivity of the resulting nano fuel mixtures, leading to increased vaporization rates of fuel droplets and improved combustion processes. The combustion of nanoparticles takes place in two stages.

During the primary combustion stage, nano-additives tend to mix with biodiesel fuel as a binding mechanism, breaking down its chemical structure and accelerating the reaction. During the secondary combustion stage, molecular oxygen present in the Mg-doped CaO structure is released (Elkelawy et al. 2021b). This released oxygen, along with higher heat, reacts with unburned hydrocarbons to increase the combustion rate. Due to the high thermal conductivity of nanofuel, fuel combustion starts earlier, resulting in higher peak pressures in the cylinder (Russell et al. 2000; Dhar et al. 2012; Soudagar et al. 2020). Figure 11, reveals that at full load conditions, the BTE of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 62.22 bar, 58.49 bar, 60.28 bar and 64.29 bar.

5.2 Effect of Mg-doped CaO Nano Additives on Heat Release Rate

The engine combustion characteristics depend on the fuel type, cylinder design, and fuel injection type which influences the heat release ate (Lei et al. 2016; Lee et al. 2019). The maximum heat release is achieved due to a lower ignition delay during combustion in a CI engine (Das et al. 2018; Alloune et al. 2018). In a CI engine, two types of combustion phases occur, the premixed combustion phase (PCP) and the diffusion phase (DP). In PCP, the overall burning rate can be determined during ignition delay period. In DP, combustion rate can be limited (Shelke et al. 2016). Figure 10 shows that heat release rate variation on Diesel, STBD25, STBD25 + 30ppm CaO and STBD25 + 30 ppm Mg-doped CaO with crank angles at ful load conditions. The heat release rate for Diesel is 54.43 $\frac{\mathrm{J}}{^{\circ}\mathrm{CA}}$, STBD25 is 37.37 $\frac{\mathrm{J}}{^{\circ}\mathrm{CA}}$, STBD25 + 30ppm CaO is 46.12 $\frac{\mathrm{J}}{^{\circ}\mathrm{CA}}$ and STBD25 + 30 ppm Mg-doped Cao is 55.32 $\frac{\mathrm{J}}{^{\circ}\mathrm{CA}}$. From the graph, it is revealed that HRR increases by 1.68%, 16.69% and 32.5%, compared with diesel, STBD25 + 30ppm CaO and STBD25.

The heat release rate dx = dw can be calculated by the following formula.

$$\frac{dx}{d\phi} = p\frac{C_P}{R}\frac{dV}{d\phi} + V\frac{C_v}{R}\frac{dp}{d\phi} + mT\frac{dC_v}{d\phi} + \frac{dQ_w}{d\phi}$$

$$\frac{dQ_w}{d\phi} = h_c A\left(T - T_w\right)$$

Here, p – Cylinder Pressure, C_p - Specific Heat @ Constant Pressure, C_v - Specific Heat @ Constant Volume, R - Gas Constant, h_c – Coefficient of Heat Transfer, A - Wall Area, and T_w - Wall Temperature.

The higher HRR of diesel fuel can be attributed to its higher calorific value leading to higher heat production during combustion. Also, due to short burn time and short ignition delay (Chandrasekaran et al. 2016; Ağbulut et al. 2022). As the concentration of Mg-doped CaO nanoadditives increases, the HRR further increases due to the enhanced ignitability. This enhanced catalytic reactivity of the resulting fuel mixture accelerates the combustion rate of the fuel precursor, thereby releasing the maximum rate of heat release (Saxena et al. 2017; Devarajan et al. 2018). This work is in good agreement with previous studies that improved HRR by attaching nanomaterials to base fuels. The reactive surface area of nanoparticles can enhance their catalytic reactivity due to their size and also increases fuel droplet spreading and fuel injection dispersion, improving combustion characteristics and fuel-air mixing (Vijay Kumar et al. 2018). At high load and high speed, the peak pressure is decreased, which could be due to the increase in friction losses resulting in reduced heat release rate.

5.3 Effect of Mg-doped CaO Nano Additives on Brake Thermal Efficiency

Brake thermal efficiency is defined as how well the heat energy of the fuel is converted into mechanical energy. It is seen from experiment that increasing engine load increases fuel consumption and increases BTE (Asokan et al. 2019). Figure 11, reveals that at full load conditions, the BTE of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 32.23%, 29.79%, 30.99% and 33.77%. BTE of STBD25 + 30ppm Mg doped CaO is found to be increased in percentage variation by 4.56%, 8.23% and 11.79% compared with diesel, STBD25 + 30ppm CaO and STBD25. The BTE of STBD25 is lower than other blends due to its higher density, higher viscosity and lower CV. The BTE of the fuel blended with 30ppm CaO is higher than that of STBD25. The use of nanoparticles converts fuels into usable energy more efficiently and improves combustion (Pandian et al. 2017; Kumar et al. 2019a, b). Therefore, the BTE of STBD25 + 30ppm Mg-doped CaO is higher than other fuel blends. The main reason for the improved performance is the additional energy generated inside the cylinder by increasing the surface-to-volume ratio of the nanoparticles (Soudagar et al. 2020). Also, the increased HRR is due to a shorter ignition delay time, and the superior ignition properties of the nanoparticle additive improve premixed combustion (Chandra Sekhar et al. 2018; Chinnasamy et al. 2019). The fuel's excellent catalytic and ignition properties result in higher peak pressures and higher instantaneous heat release during the combustion process. When nanoparticles are added, the fuel droplets become smaller, the fuel becomes less viscous, and more effective fuel surface area is exposed (Vijay Kumar et al. 2018). The improved combustion parameters of nanoparticles are due to their ability to release oxygen atoms from the lattice during combustion (Barzegar et al. 2019; Çelĭk and Bayindirli 2020).

5.4 Effect of Mg-doped CaO Nano Additives on HC Emission

There are various possible sources for unburned hydrocarbon formation in CI engines. Fuel trapped in nozzle, crevice areas and cylinder piston interface accounts for the majority of HC emission (Anchupogu et al. 2018; Tang et al. 2021). Other factors include incomplete evaporation of fuel mixture, local over rich/over lean mixture and liquid wall film interface with more spray impingement, high viscosity of the fuel (Koegl et al. 2018). It is observed from the experiments, It can be seen that HC emissions increase with increasing loads owing to more fuel entering into the combustion chamber thus resulting in several rich mixture zones, poor combustion, thus emitting higher unburnt fuel fractions, i.e. higher HC emissions (Raheman and Kumari 2014; Yesilyurt et al. 2020). The presence of inbuilt O_2 in biodiesel blend helps in sustaining the combustion thus resulting in lowered HC emissions for CaO and Mg-doped CaO Nano-additives blended STBD25. CaO and Mg-doped CaO Nano-additives improved the fuel injection and leads to better atomization of fuel due to lower viscosity, increasing the surface to the volume ratio of nanoparticles, and enhancing the heat-transfer rate.

Figure 12, reveals that at full load conditions, the HC emission of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 25 ppm, 23 ppm, 21.89 ppm and 20.64 ppm. On comparison, it is revealed that HC emission for STBD25 + Mg doped CaO decreased by 21.12%, 6.06% and 11.43% compared with diesel, STBD25 + 30ppm CaO and STBD25. Lower HC emissions were also observed due to higher catalytic activity and higher surface-to-volume ratio resulting in improved combustion (Vijay Kumar et al. 2018). The addition of nanoparticles lowers the activation temperature of carbon combustion and improves fuel oxidation (Vairamuthu et al. 2016). The nanoparticles act as an oxygen buffer, providing supplemental oxygen that facilitates the formation of a stoichiometric mixture within the combustion chamber.

5.5 Effect of Mg-doped CaO Nano Additives on CO Emission

HC emission and CO are affected by high viscosity, poor fuel-air mixture, less oxygen content, poor vaporization and incomplete combustion (Raheman and Kumari 2014; Yesilyurt et al. 2020). At partial load, CO emissions are high. However, CO emissions increase with increasing engine load and it will be highest at full load conditions. CO emissions are influenced by engine load, fuel consumption and oxygen availability (Sendzikiene et al. 2006). In nature, biodiesel has higher oxygen content compared to raw diesel. Hence CO emission is lower for biodiesel compared to fossil fuels (Arbab et al. 2015). The presence of nanoparticles in biodiesel results in improvement of fuel air mixing, improved ignition characteristics and higher surface-to-volume which improve fuel droplets size that leads to complete combustion and reduction in CO. Figure 13 reveals that at full load conditions, the CO emission of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 0.06%, 0.03%, 0.03% and 0.02%. Lower viscosity improves fuel atomization and plays an important role in reducing CO emissions. The reactive surface of the nanoparticles supports reactivity as a potential catalyst and improves fuel atomization. Nanoparticles reduce the homogeneity of the base fuel composition and cause more decomposition during fuel injection. STBD25 + 30 ppm Mg-doped CaO biodiesel reduces CO emissions from 33–67% compared to diesel and other blended fuels.

5.6 Effect of Mg-doped CaO Nano Additives on NOx Emission

NOx production is driven by peak cylinder temperatures, oxygen availability, and ignition delay (Panneerselvam et al. 2016). Due to the high oxygen content of biodiesel, NOx emissions are high. Increasing the proportion of nanoparticles decreased NOx emissions (Karthikeyan and Prathima 2017; EL-Seesy et al. 2018). This is due to the presence of oxygen-containing additives, which improved combustion. The addition of CaO metal oxide nanoparticles leads to complete combustion as it acts as an oxygen catalyst. In such cases, maximum heat release rates and high peak pressures during combustion are to be expected. EGT is directly proprtional to NOx content. This indicates that increased EGT plays an important role in NO production (Yadav et al. 2018; Elkelawy et al. 2021a). Lower ignition delay of Mg-doped CaO nanoparticles reduced premixed combustion rate which in turn decreased incylinder temperature during combustion and reduced NOx emissions. Mg will retreat CaO from decomposition and retain its original form for longer period. Hence oxygen taking part in combustion is stable and so the combustion temperature, hence NOx emission is reduced. Addition of Mg-doped CaO nanoparticles to STBD25 biodiesel reduced NOx emissions compared to the STBD25 biodiesel blend due to the catalytic charactistics of the nanoparticles.

$$\mathrm{Mg.\,CaO} + 2NO_2 \rightarrow Mg\left(NO_2\right)_2 + \mathrm{CaO}$$

Figure 14, reveals that variation of the NOx emission of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO at full load conditions. As engine load increases, NOx emissions also increases due to increase in combustion characteristics and adiabatic flame temperature. The NOx emission of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 1010 ppm, 1224 ppm, 1311.53 ppm and 1105.47 ppm. The NOx emissions of the STBD25 + 30ppm CaO is higher than all other fuel belnds. NOx released while using STBD25 + Mg-CaO in CI engine was observed to decrease compared with STBD25 and STBD25 + CaO (by 10.72% and 18.64%) and increase compared with diesel (by 8.64%). Whereas an insignificant drop in NOx was observed while using STBD25 + Mg doped CaO compared with STBD25 + CaO and STBD25 despite a significant increase in HRR and BTE which might be due to the capture of excess oxygen by Mg during the combustion diffusion phase.

5.7 Effect of Mg-doped CaO Nano Additives on Smoke

Figure 15 shows the evolution of smoke emissions for diesel, STBD25, STBD25 + 30CaO and STBD25 + 30Mg-doped CaO under full load conditions and constant engine speed. For diesel and all other biodiesel blends, smoke emissions increase with engine speed. The effects of CI engine exhaust smoke are due to incomplete combustion, low oxygen utilization, fuel carbon content (compared to diesel), and rich mixing zones. Delayed ignition results in a large accumulation of fuel in the cylinder, slowing the oxidation of CO to CO2 and increasing soot concentrations. The premixed combustion stage burns a rich mixture for a short time, resulting in higher CO emissions than the diffusion stage (Mishra et al. 2017; Venu et al. 2019). Smoke emissions from biodiesel are generally lower than emissions from fossil fuels due to the built-in oxygen. Furthermore, the addition of nano-additives to biodiesel reduces smoke generation due to its catalytic activity. The effects of nano-additive reduce smoke due to additive surface area, good automation of fuel, complete combustion, and higher chemical activity (Annamalai et al. 2016).

Nanoparticles increase the catalytic activity (combustion reaction) during the combustion process, resulting in less smoke. Figure 15 reveals that at full load conditions, the smoke emission of diesel, STBD25, STBD25 + 30ppm CaO, and STBD25 + 30ppm Mg doped CaO are 5.13 FSN, 3.97 FSN, 3.63 FSN and 3.32 FSN. The smoke was observed to decrease by 19.58%, 9.34% and 54.52% compared with STBD25 and STBD25 + CaO and diesel.

Conclusion

The current study aims at a new approach to the effects of Mg-doped Cao in biodiesel from Sapindus trifoliatus (STBD25). Experiments were performed using four different samples such as raw diesel, STBD, STBD25 + 30ppm CaO, and STBD25 + 30ppm with Mg-doped CaO nano-additives. Experiments were conducted with a bTDC injection timing of 23 degrees, 18:1 compression ratio and an injection pressure of 220 bar using a 4-stroke single-cylinder. The following conclusions are drawn based on experimental results.

- Extraction of oil from *Sapindus Trifoliatus* kernel is investigated and the yield was about 51.4 to 55.3wt %.
- Synthesis of Mg doped CaO heterogeneous catalyst is investigated and used as catalyst in biodiesel extraction and as nano additive in biodiesel.
- A maximum biodiesel conversion of 91.75% was achieved at 58°C, 73 min with a catalyst concentration of 4% (w/w) and a methanol: oil molar ratio of 15:1.
- STBD25 + 30Mg doped CaO increases the (i) in-cylinder pressure by 3 to 9%, HRR by 1.5 to 33%, BTE by 4 to 12% (ii) decreases the UHC by 6 to 21% and CO by 0.01 to 0.04% compared with diesel, STBD25 + 30ppm CaO and STBD25.
- Whereas an insignificant drop in NOx was observed in spite of a significant increase in HRR and BTE which might be due to the capture of excess oxygen by Mg during the diffusion combustion phase.

Declarations

Ethical Approval

NO human and/ or animal are used for studies.

Competing interests

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Authors' contributions

Kota Muninathan: Conceptualization, Methodology, Data curation, performed experimental work Investigation, Writing Original Draft and Visualization.

Madhavan Venkata Ramanan: Writing - review & editing, Supervision and Project Administration.

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Consent to Participate

Not Applicable

Consent to Publish

Not Applicable

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Figures

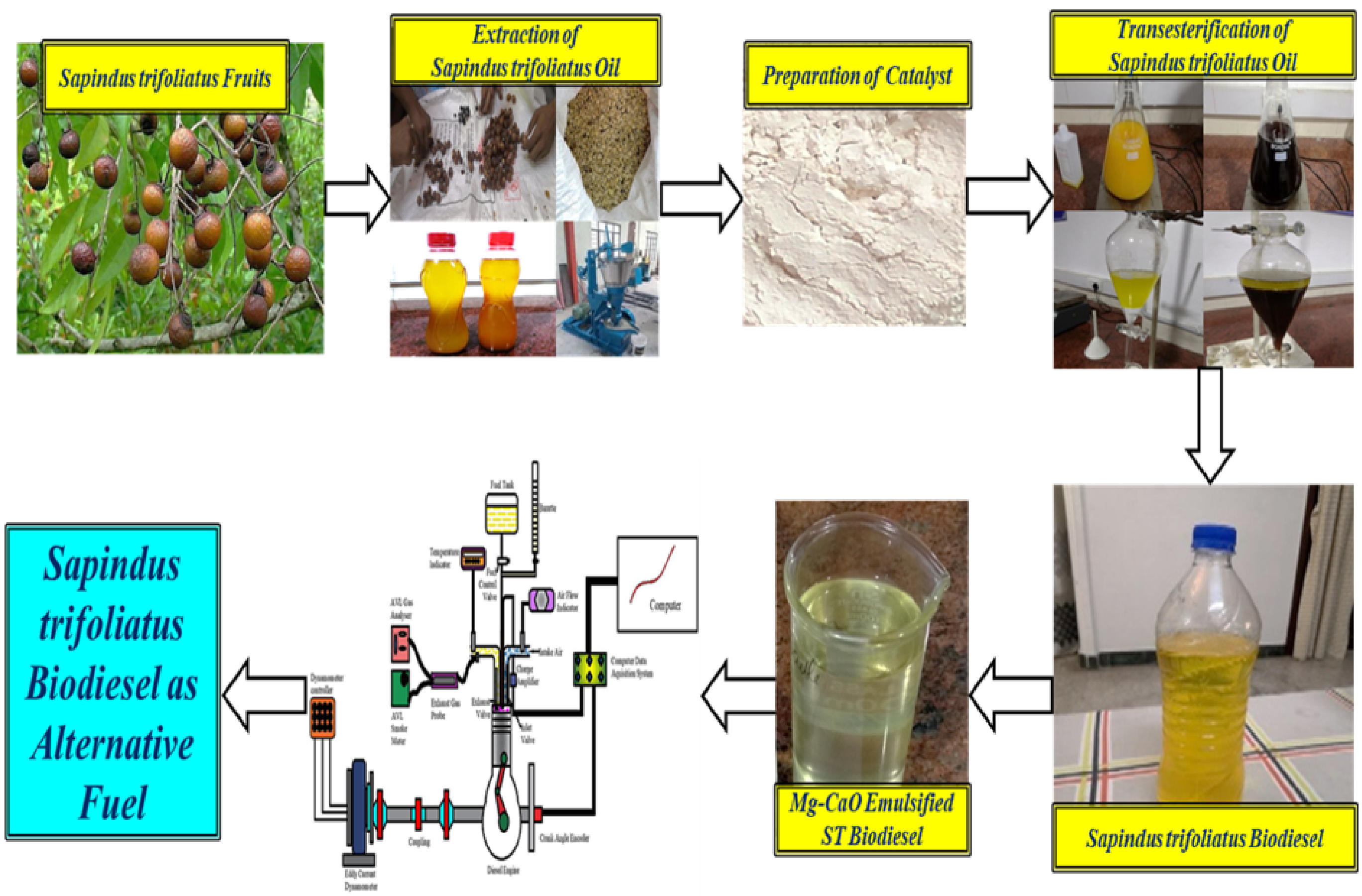


Figure 1

Stages of work for the current experimentation

Figure 2

Workflow carried out in the oil extraction

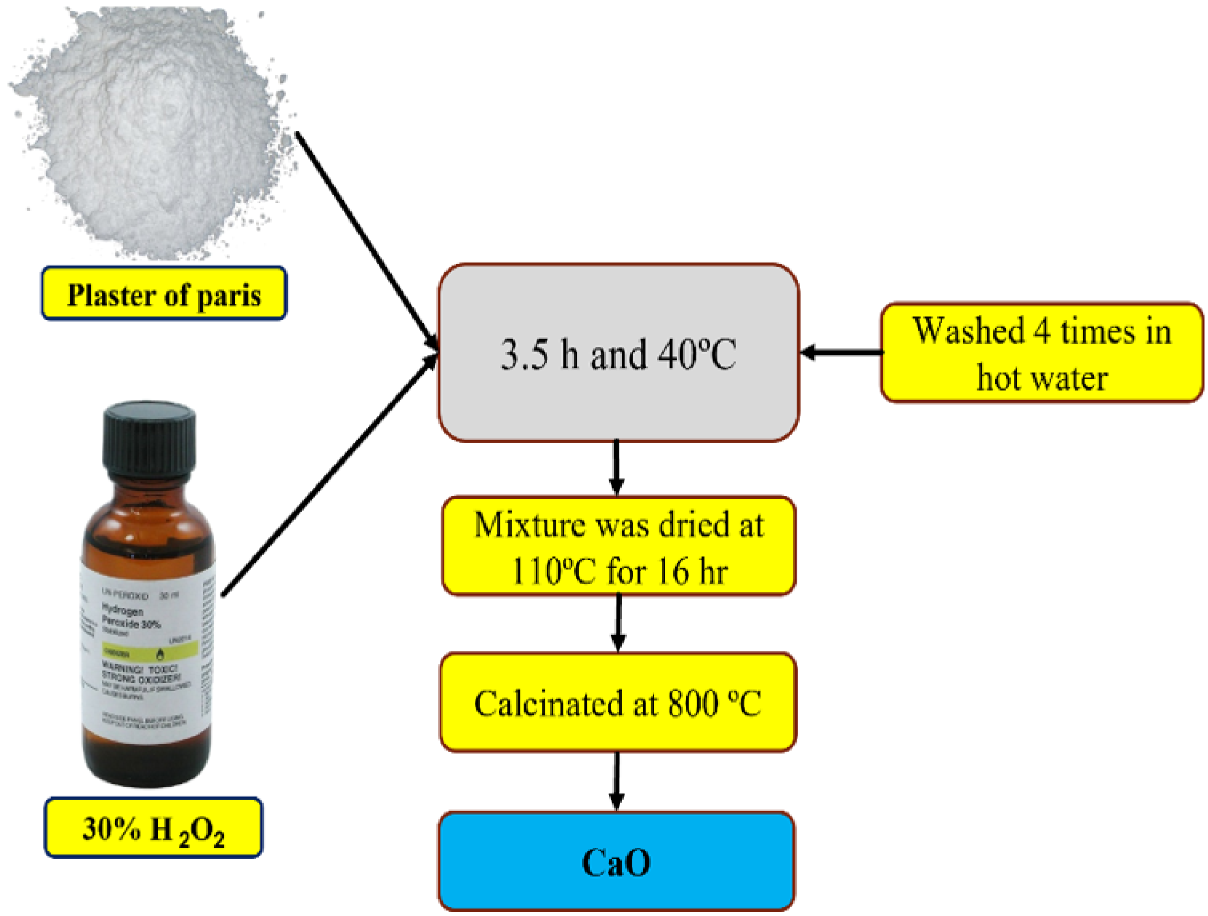


Figure 3

Preparation of Calcium Oxide using Plaster of Paris

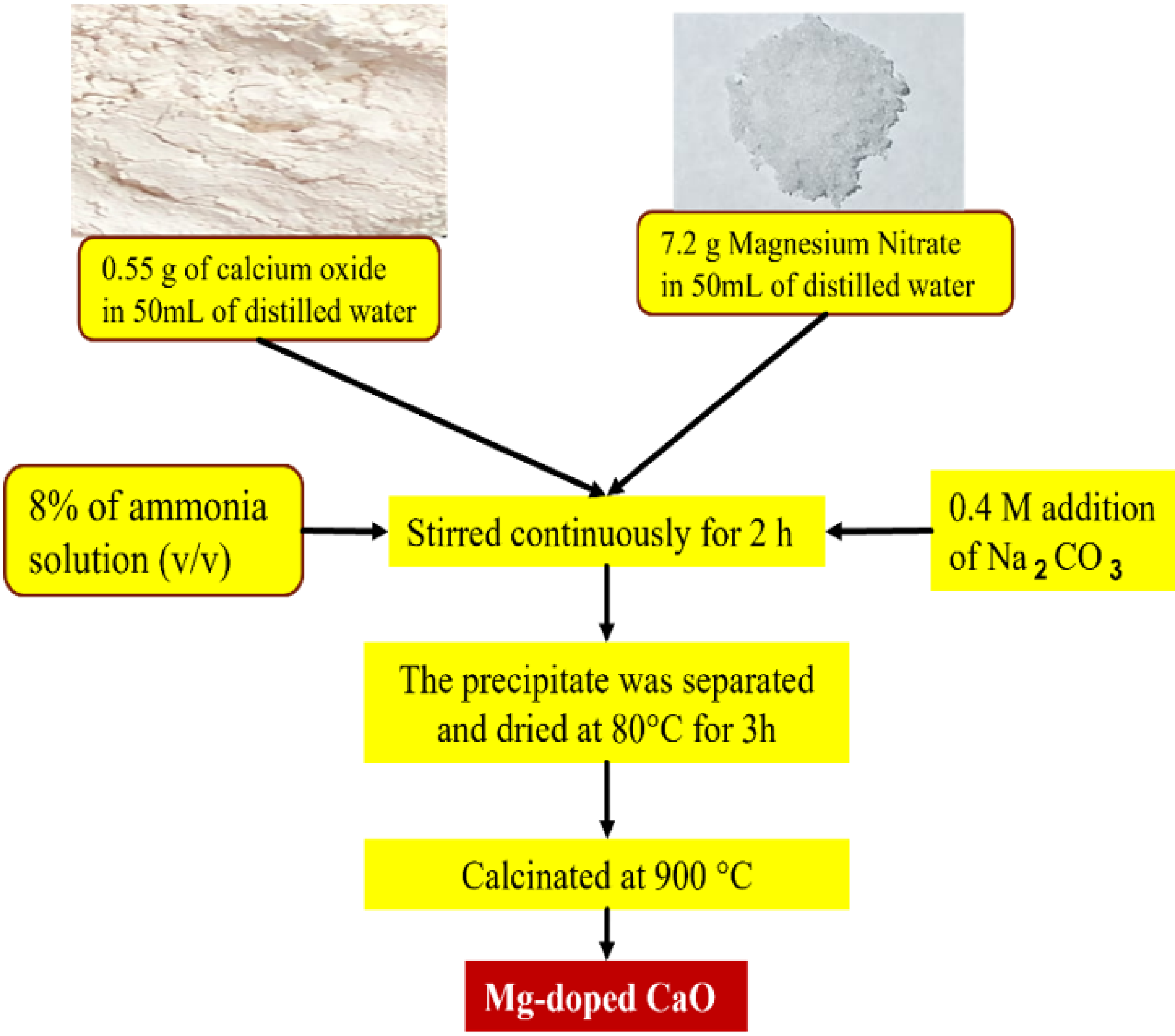


Figure 4

Synthesis of Mg-doped CaO Catalyst

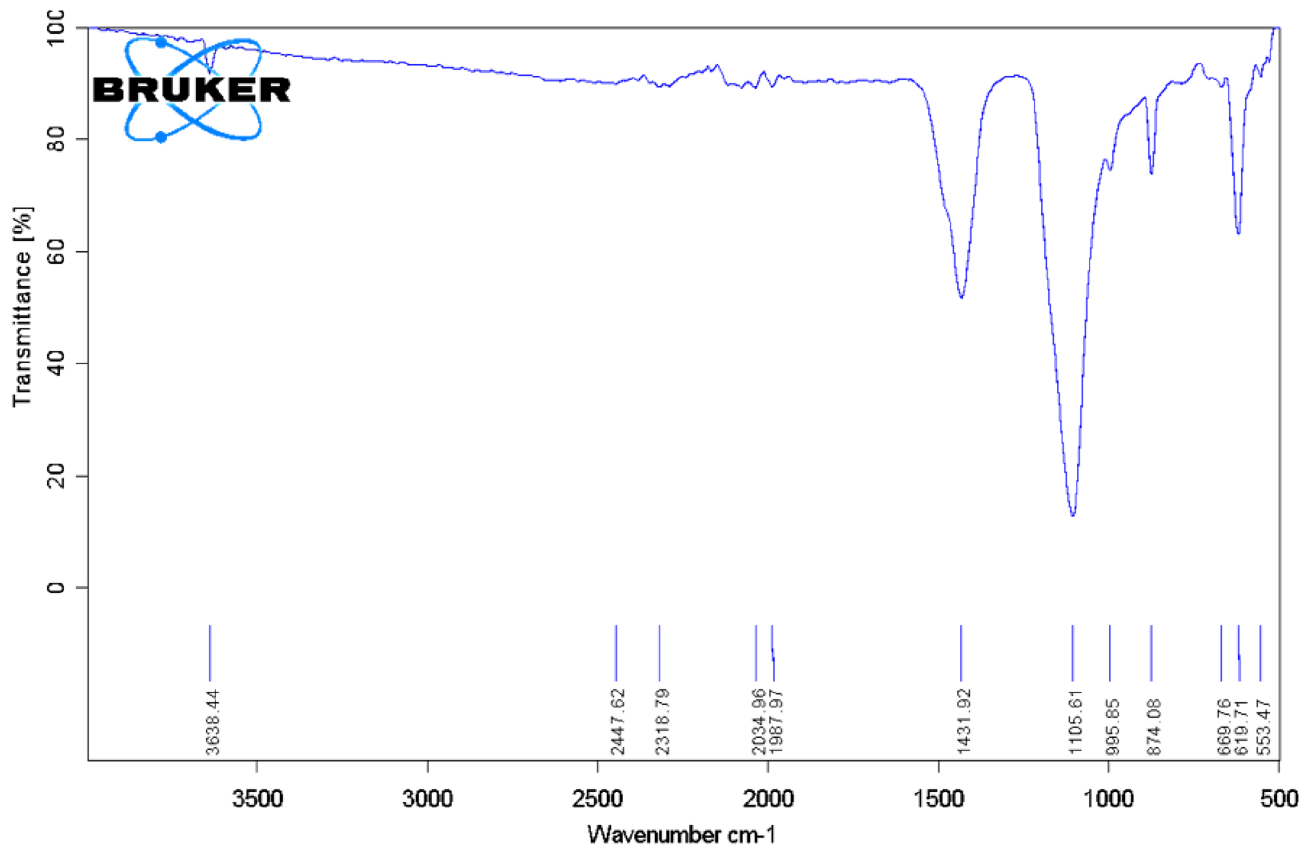


Figure 5

FTIR plot of Mg-doped CaO catalyst

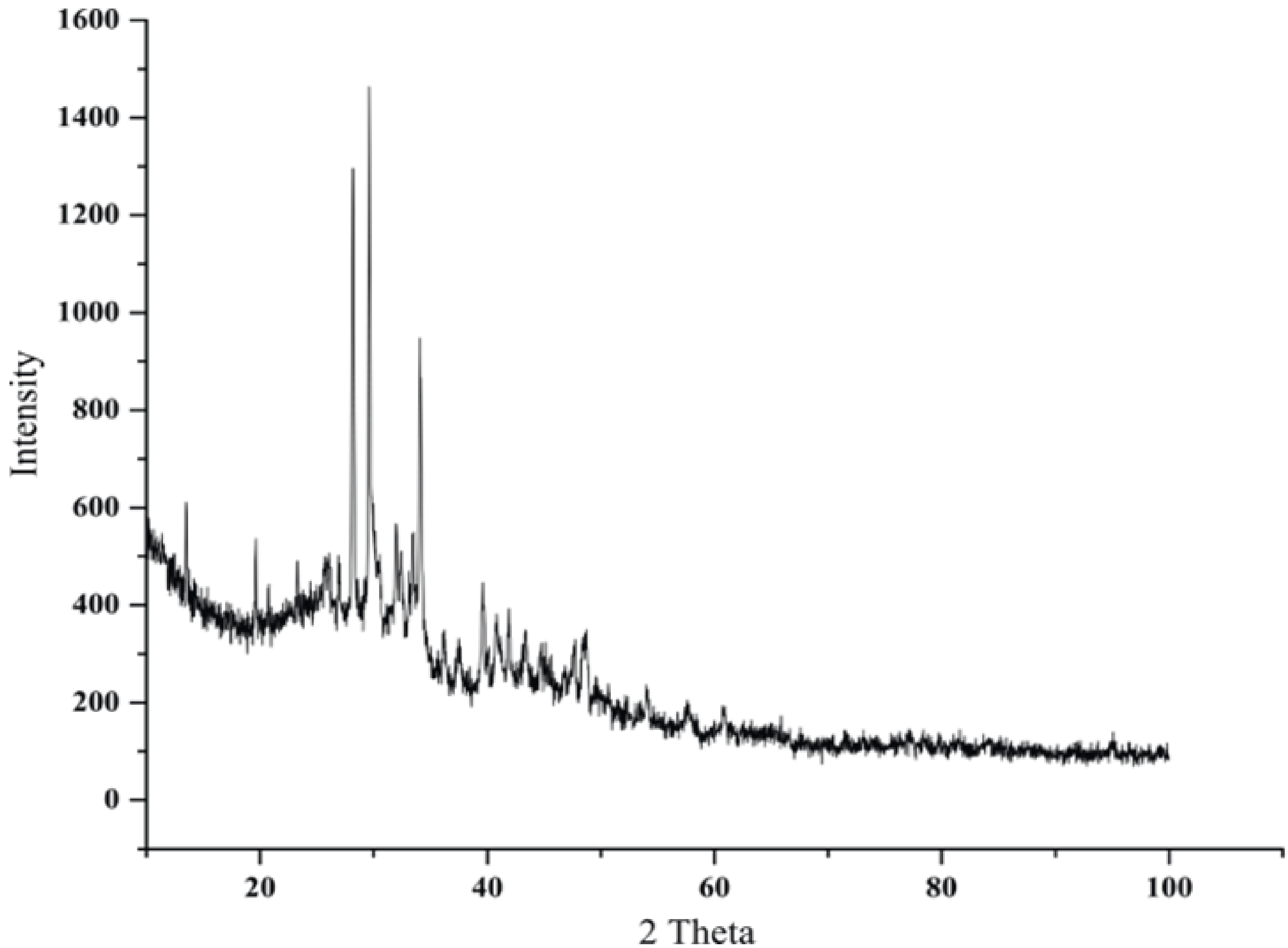


Figure 6

XRD plot of Mg-doped CaO catalyst

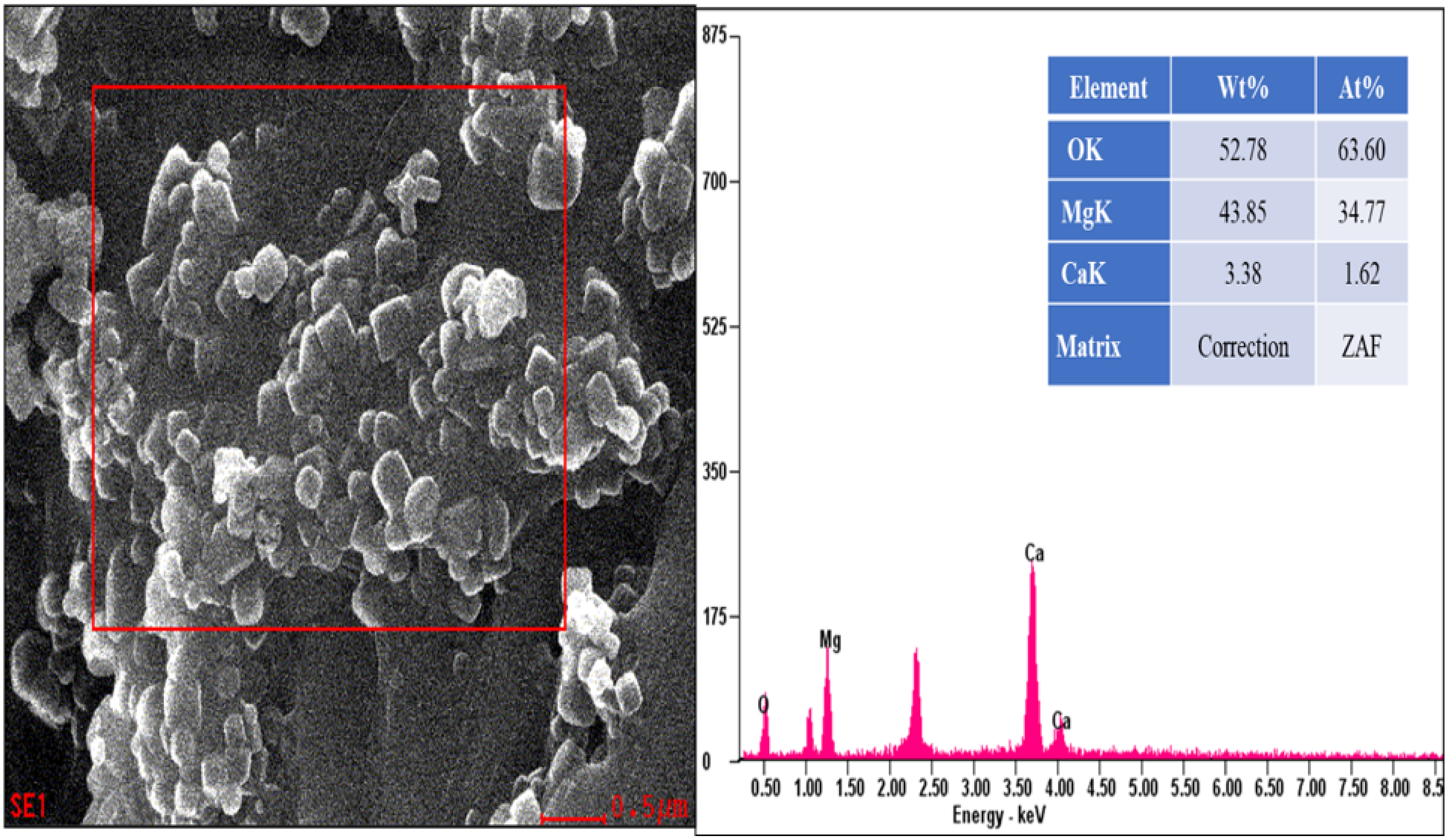
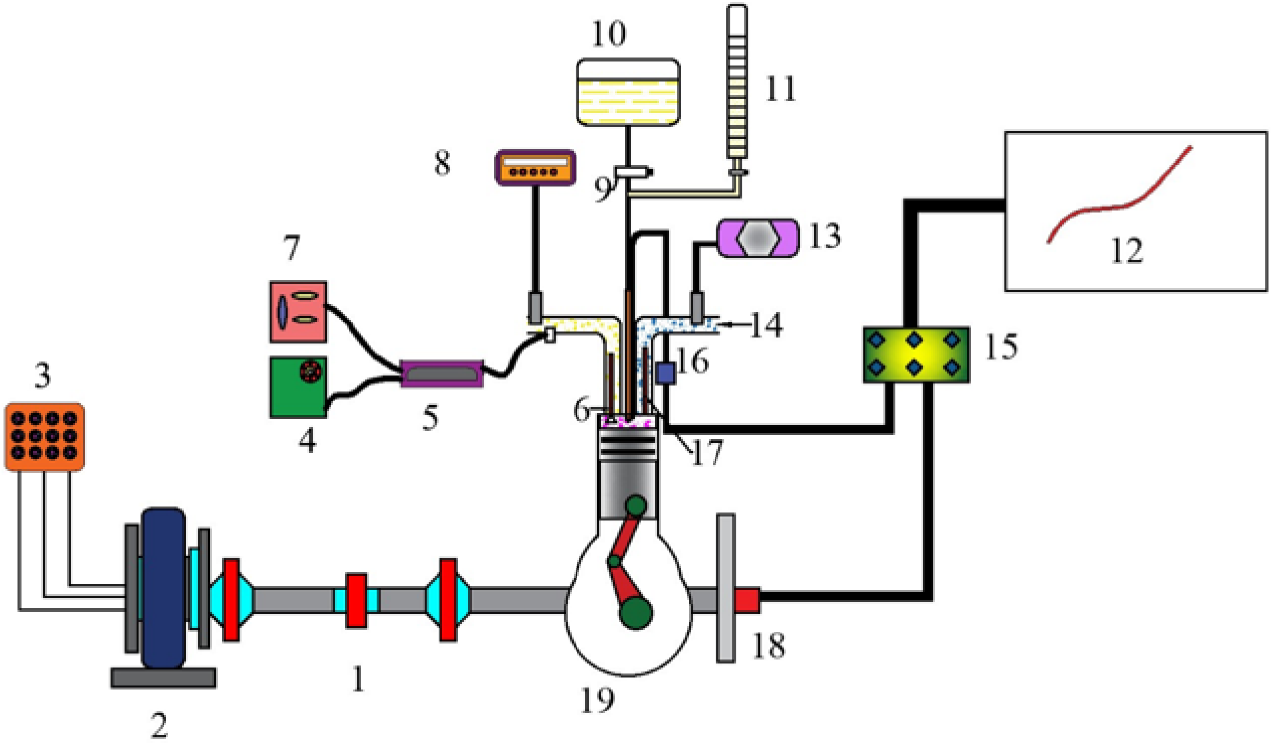


Figure 7

SEM plot of Mg-doped CaO catalyst



1	Coupling	11	Burette
2	Eddy Current Dynamometer	12	Computer
3	Dynamometer controller	13	Air Flow indicator
4	AVL Smoke Meter	14	Intake air
5	Exhaust Gas Probe	15	Computer Data Aquisition System
6	Exhaust Valve	16	Charge amplifier
7	AVL Gas Analyser	17	Inlet valve
8	Fuel control valve	18	Crank Angle Encoder
9	Temperature Indicator	19	Diesel Engine
10	Fuel Tank		

Figure 8

Schematic of the Engine Setup.

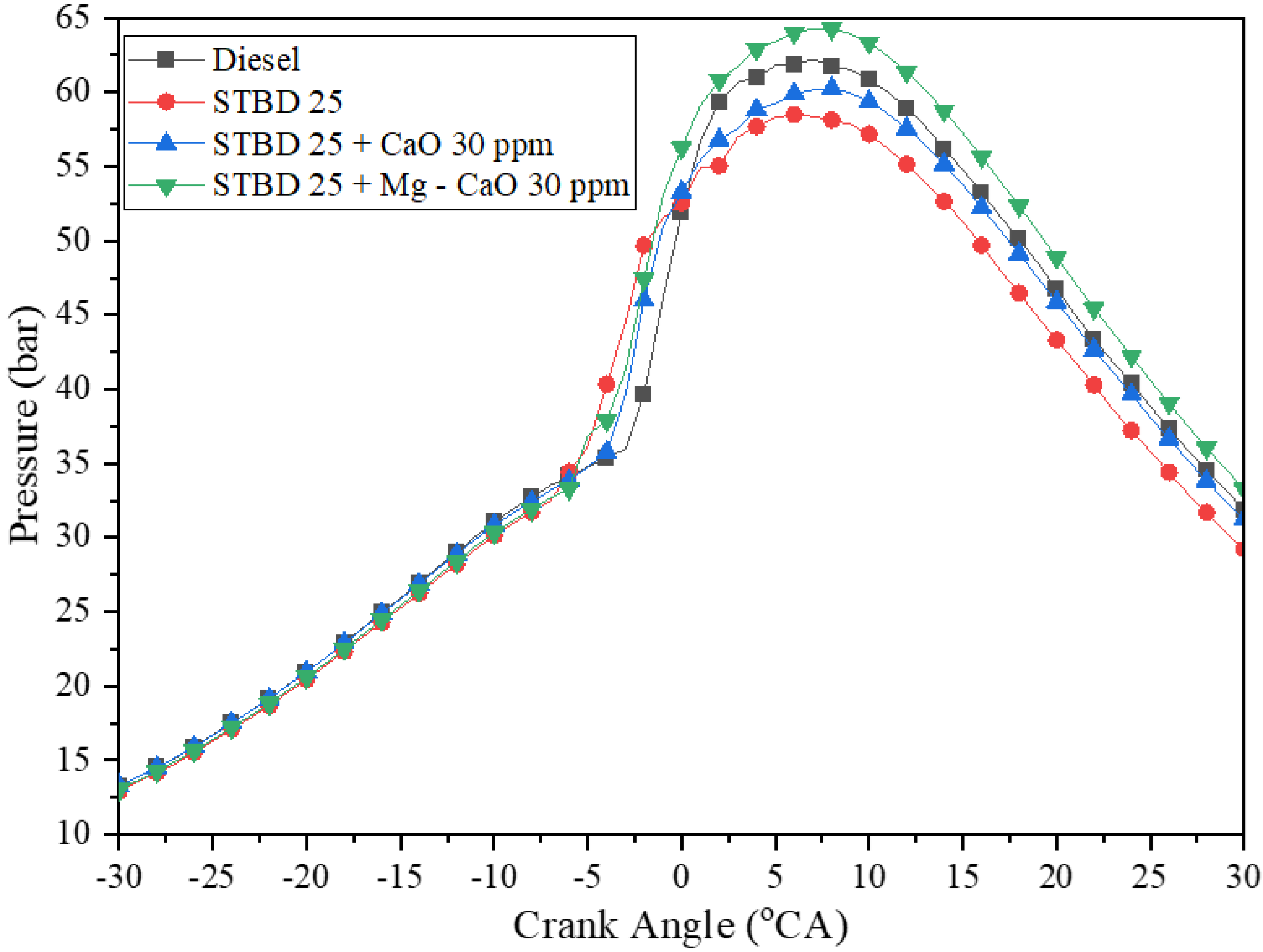


Figure 9

Effect of Mg doped Cao on In-Cylinder Pressure variation

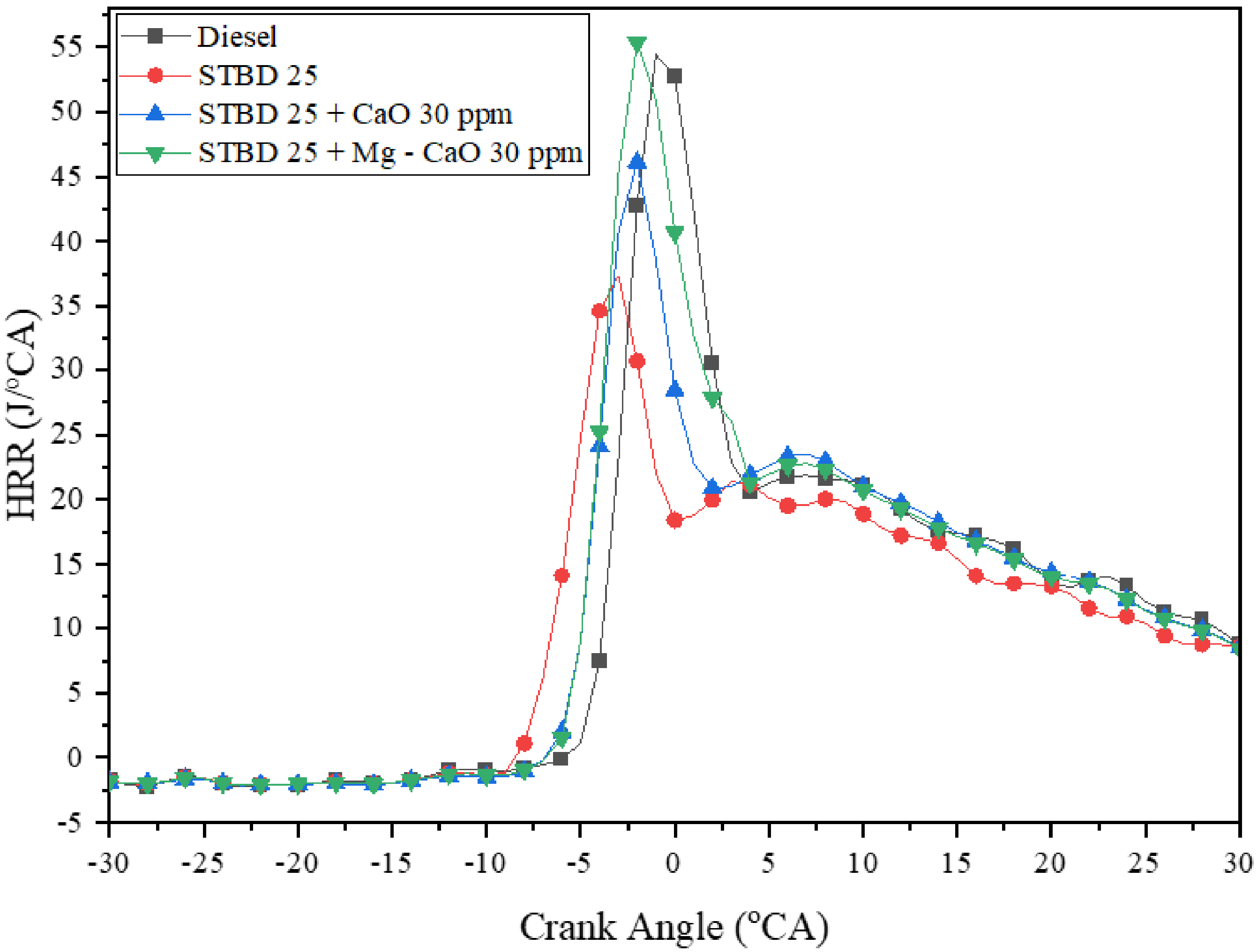


Figure 10

Effect of Mg doped Cao on Heat Release Rate variation

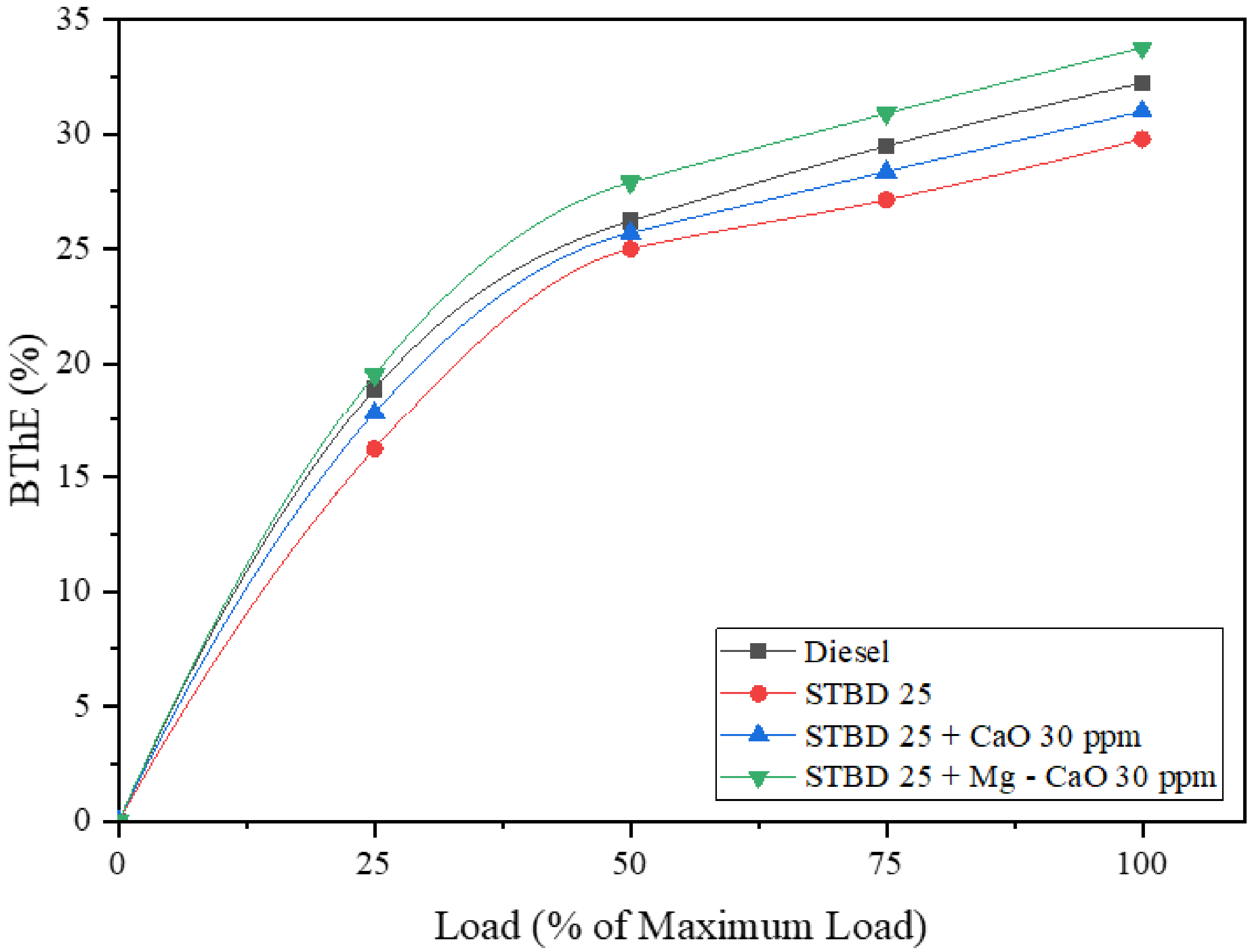
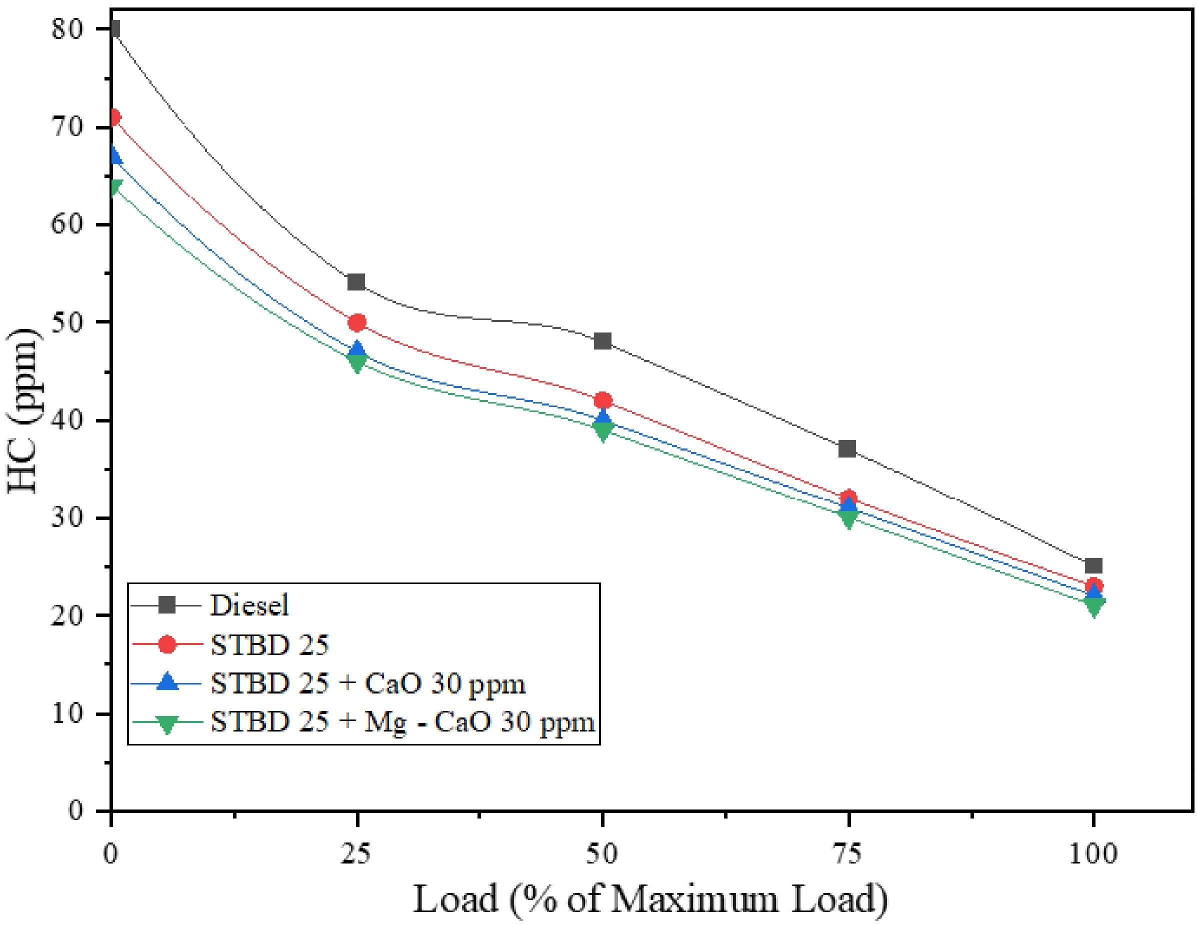


Figure 11

Effect of Mg doped Cao on Brake Thermal Efficiency



HC (ppm)
80
70
60
50
40
30
20
10
0
0
25
50
75
100
Load (% of Maximum Load)
Diesel
STBD 25
STBD 25 + CaO 30 ppm
STBD 25 + Mg - CaO 30 ppm

Figure 12

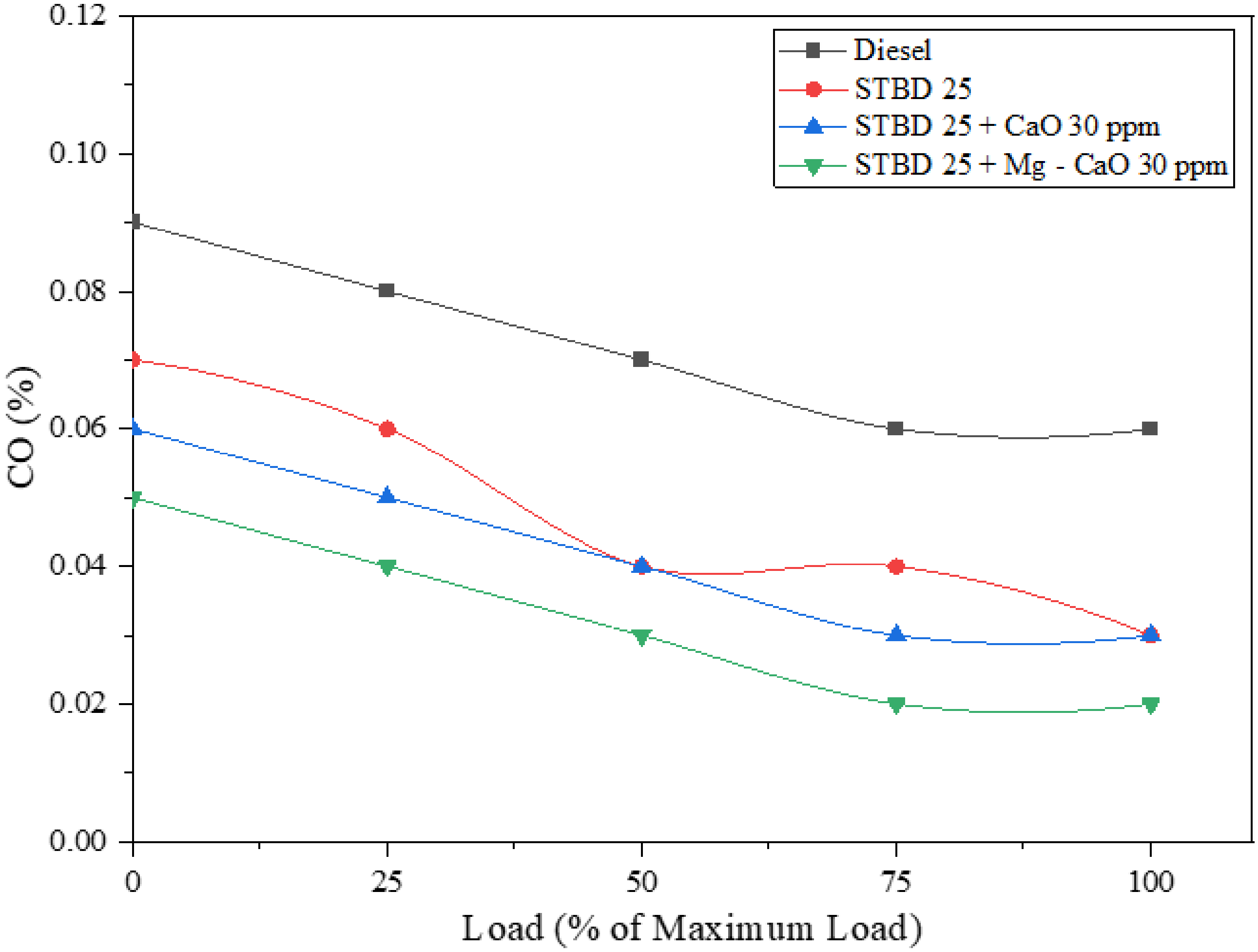


Figure 13

Effect of Mg doped Cao on HC Emission

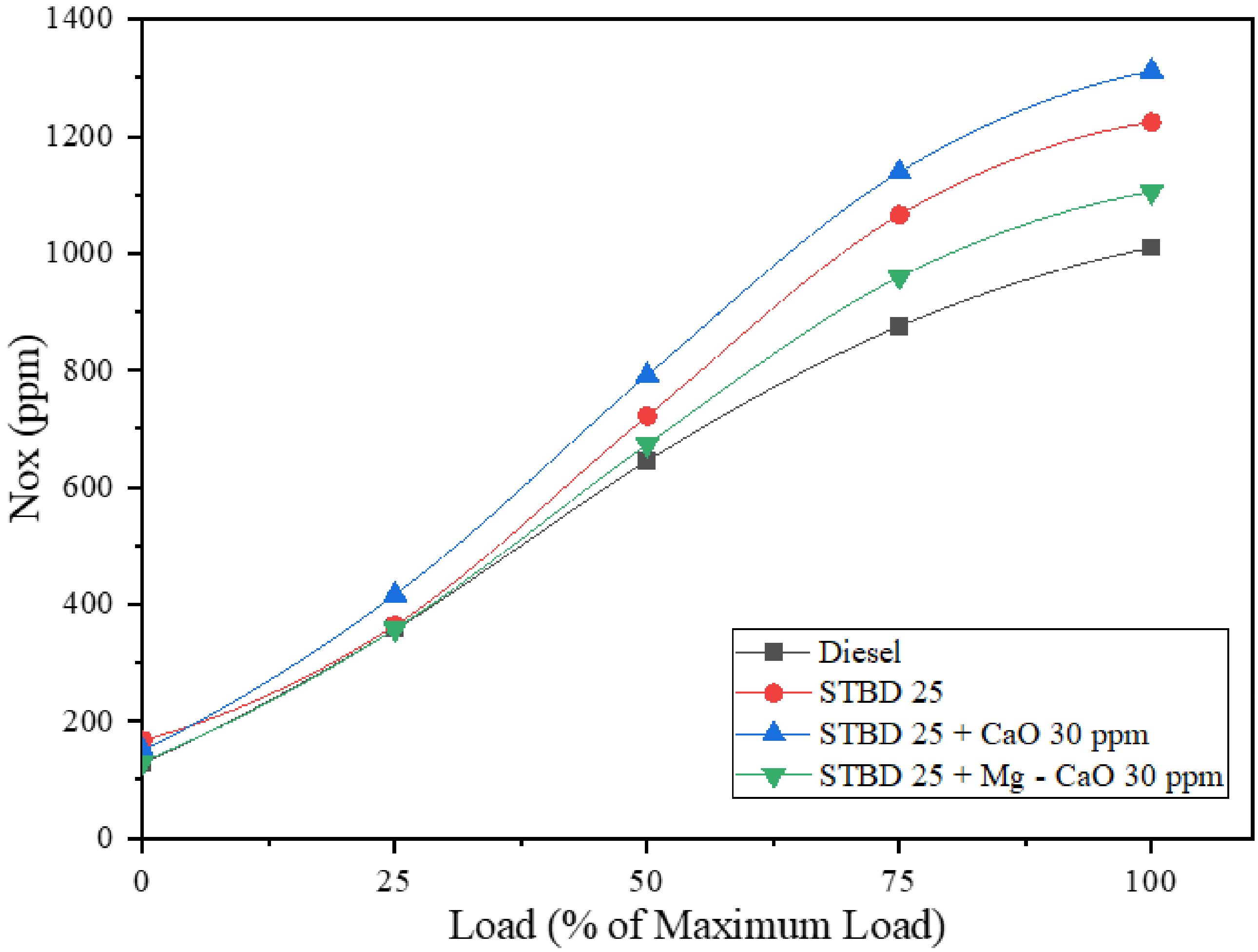


Figure 14

Effect of Mg doped Cao on NOx Emission

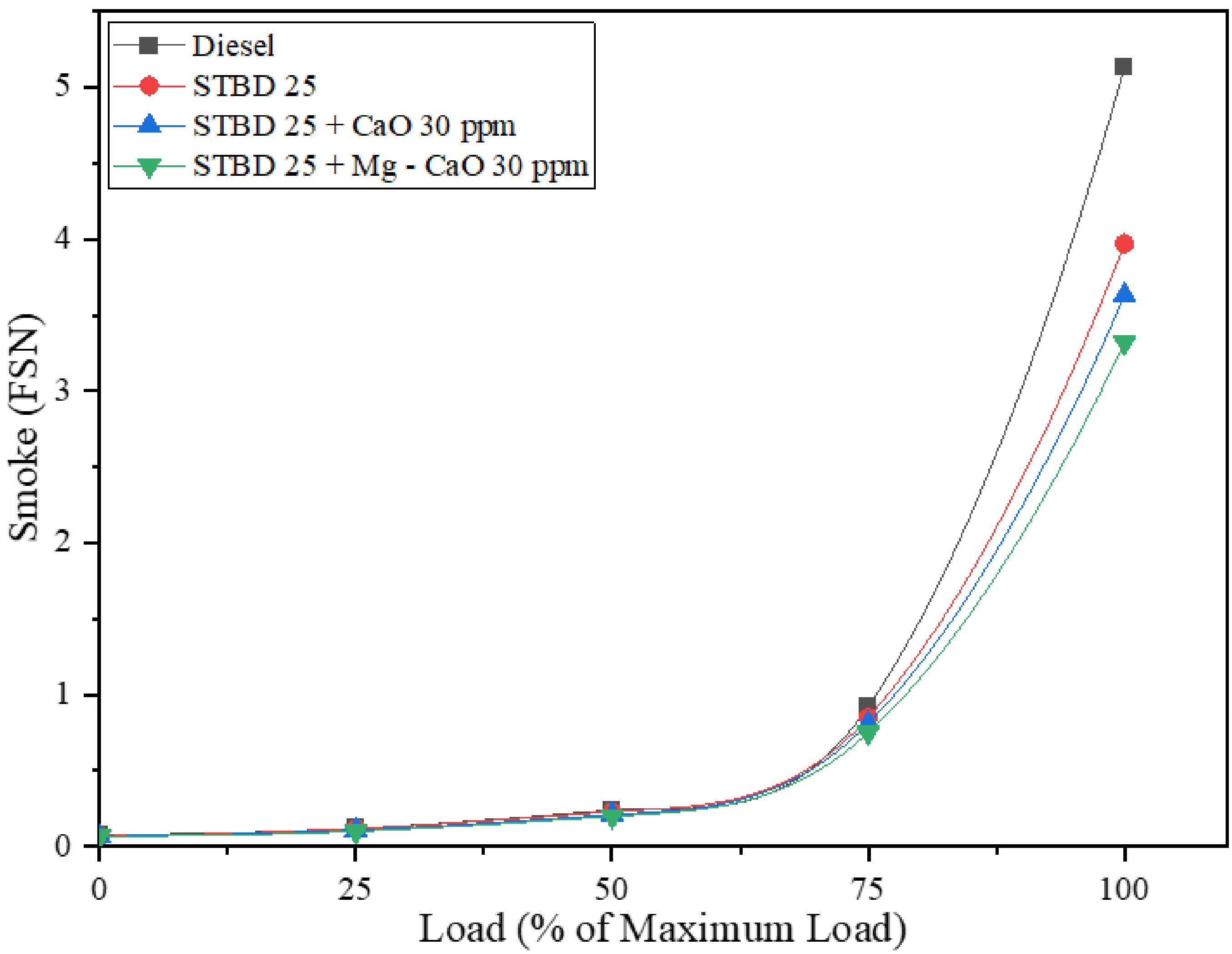


Figure 15

Effect of Mg doped CaO on Smoke