Carbon Dioxide Capture using Adsorption Technology in Diesel Engines

S. Saravanan*, C. Ramesh Kumar*‡

*Department of Automotive Engineering, Vellore Institute of Technology, India - 632014
(muthusaravanan92@gmail.com, crameshkumar@vit.ac.in)

‡ C. Ramesh Kumar; Department of Automotive Engineering, Vellore Institute of Technology, India - 632014; Tel: +90 989 418 9439,
crameshkumar@vit.ac.in

Received: 09.10.2020 Accepted:05.11.2020

Abstract- Diesel engines are the major sources of Carbon dioxide (CO_2) emission in the transport sector compared to petrol engines. The current trend in diesel engine research is shifting towards the reduction of CO_2 emissions. Removal of CO_2 from the engine exhaust and recycling it in industrial applications could be a better solution for CO_2 reduction. Out of a few methods available, adsorption and desorption of the CO_2 using zeolite is an economical way to remove CO_2 from the engine exhaust. In this study, CO_2 from the exhaust of a Kirloskar TAF AV1 type diesel engine is captured using zeolite 13X. To optimize the capture of CO_2 from the engine exhaust, three quantities of zeolite are considered. A 100, 150 and 200 grams of zeolite are stored in a cylindrical chamber and placed in the exhaust line of the engine. The surge tank is connected before the zeolite chamber to reduce the backpressure of the engine caused by the addition of zeolite chamber. Emissions such as CO_2, Unburned hydrocarbon (HC) and Carbon monoxide (CO) before and after the chamber are measured to evaluate the CO_2 adsorption capacity of the zeolite 13X. From the results, it was found that low-cost zeolite sieves can adsorb upto a maximum of 45% of the CO_2 emission from the engine exhaust.

Keywords Adsorption, desorption, carbon dioxide, diesel engine, emissions, zeolite.

1. Introduction

Growing population and substantial economic growth, create an enormous demand for fossil fuel energy utilization in various sectors like transportation, aviation, industrial, and non-industrial applications [1, 3]. Diesel is the commonly used fossil fuel in transport and non-transport applications. Combustion of fossil fuels is the source of global warming, ozone depletion and certain natural disasters. Diesel engines are the major sources of atmospheric pollutions. Several developing countries have banned the operation of old diesel vehicles due to increased environmental deterioration. are increasing day by day. Researchers are rigorously trying to cut down these issues by importing alternate fuels [4, 6]. Biodiesel is an alternate source to reduce emissions without changing the existing engine [7]. Meanwhile, only 10% of biodiesel can be blended with conventional diesel to attain maximum performance. However, retarded thermal efficiency and higher NO_x emission are drawbacks of biodiesel implementation [8, 10]. Energy policy reviews state that Carbon dioxide (CO_2) emissions are majorly contributed by three entities such as transportation, industry and buildings. Transportation and industries together generate 50% of CO_2 emissions whereas the buildings alone contribute 50% of the total CO_2 generated [11]. Because of the large number of buildings and building infrastructures such as air-conditioners, refrigerators, lighting, elevators, etc the energy consumption of the buildings is very high. As electricity is derived from thermal power plants, CO_2 generation by buildings is very high. Figure 1 shows the worldwide CO_2 emissions by various countries, surveyed by the Environmental Protection Agency of USA. Amongst several nations, USA is the major contributor to the CO_2 emission followed by China, Russia, Japan and India respectively. Diesel engines are the major contributors to CO_2 emissions in the transport sector. On average, diesel engines emit 9.5% higher CO_2 than petrol engines [12]. United States Environmental Protection Agency says a typical passenger vehicle emits about 4.6 metric tons of carbon dioxide per year. Every gallon of fuel burned creates about 8,887 grams of CO2. The billions of vehicles which are still operating contribute to the climate change. Apart from engine size and utilization, a single diesel vehicle emits 34.8 tonnes of CO_2 in its lifetime accounting from fuel extraction to wheel power processes. Compared to the modification of the existing engine design and hardware using several post-combustion and pre-combustion technologies to reduce CO_2 emission, capturing and reuse of the CO_2 emissions found to be easy and best way to reduce emissions. The pressure swing adsorption technique seems to be possible [13, 14]. Carbon nanotubes, organic porous foams, and zeolites are some of the commonly used materials to adsorb CO2 emissions [15, 16].

Zeolites are molecular sieves used in the desiccating industrial gas processing for removing impurities in the air separation unit. They are aluminosilicate crystalline materials with a distinct Si/Al ratio connected by oxygen atoms (SiO_2/Al_2O_3). Zeolites were processed by the Plackett-Burmann method and evaluated based on effectiveness. Zeolite 13X is represented by the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot H_2O$ [17]. Zeolite such as ZSM-5, 13X and 5X are types commonly available in the market with different pore sizes [18, 19]. Compared to ZSM-5 and 5X, zeolite 13X has a strong CO_2 adsorption capacity. The zeolites can be reused again after regeneration and saturation. In industries, CO_2 is captured by selective gas screening and scrubbing technologies which require a large quantity of energy and water. Broadly, adsorption techniques using zeolites are portable and efficient systems to reduce CO_2 emissions [20].

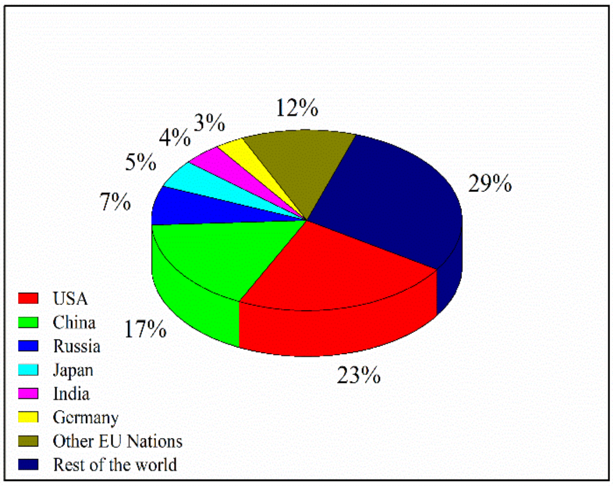

Fig. 1. CO_2 emission by nations.

Arunkumar Samanta et al [13] reviewed different types of CO_2 capturing technologies and materials. The review highlights the techniques and materials which utilize lesser energy for CO_2 sequestration. Jerome merel et al investigated the effects of zeolite 5A and 13X in adsorption technologies. The adsorbing temperature is kept as a varying parameter to determine the optimum temperature and mass of zeolites required for the trial. From the experiments, it was found that selectivity for zeolite 5A is 90 and 13X is 96. This concludes that zeolite 13X is better compared to 5A [19, 21].

In addition to the research related to the CO_2 adsorption capabilities of different Zeolite materials, gravimetric analysis of CO_2 adsorption in zeolite is also studied through numerical and experimental methods by various researchers and related literature are available. From the literature, it was identified that a hybrid temperature- vacuum pressure swing adsorption system proves to be feasible compared to thermal swing [22, 23] and pressure swing adsorption system. Before experimentation information concerning the adsorption equilibrium analysis is significant. To determine the mass of CO_2 adsorbed and desorbed there are various isotherms and governing equations that have been investigated by researchers [24]. Amongst them, Toth isotherm, UNILAN and Sips correlations agree with most of the investigations. These models or equations are derived to find the adsorption equilibria of CO_2 microporous adsorbents. The toth isotherm is a semiempirical relation used to correlate the experimental CO_2 adsorption data. It is a three-parameter model and expressed as Eq. (1).

$$q = \frac{q_s P}{\left(b + P^t\right)^{1/t}} \tag{1}$$

Where q is the mass of CO_2 absorbed per unit mass, P is the equilibrium pressure, q_s, b and t are isotherm parameters [16]. Using the above equation the mass of zeolite bed required for the exhaust can be determined [25]. The Toth isotherm is an equation that numerically describes various systems with sub-monolayer coverage. The Toth equation is used for fitting data for many kinds of adsorbates including activated carbons and zeolites because of its simplicity. However, the results are accurate only at high temperatures. The UNILAN model is another empirical relation to correlating the adsorption equilibria and it is given as stated in Eq. (2).

$$q = \frac{q_s}{2s}\,\ell\left(\frac{c + P\,e^{+s}}{c + P\,e^{-s}}\right) \tag{2}$$

Where q_s, c and s are isotherm parameters. The results of UNILAN model seem larger at higher temperatures than the Toth equation. Considering both the problems in Toth and UNILAN equation a new model is proposed based on Freundlich equation. The model is named Sips model and is displayed in Eq. (3).

$$q = \frac{q_s\, b\, P^{1/n}}{1 + b\, P^{1/n}} \tag{3}$$

Where q_s, b and n are isotherm parameters [25]. Based on the above said Sips model the adsorption equilibria of CO_2 for zeolite 13X at 25 and 50° C with respect to pressure is shown in Fig. 2 [26]. From the Fig. 2 it is evident that temperature plays a major role compared to the pressure in CO_2 adsorption. Overall, the adsorption system is cost-effective compared to commercially available three-way catalysts. The present investigation evaluates the CO_2 adsorption characteristics of zeolite 13X molecular sieves.

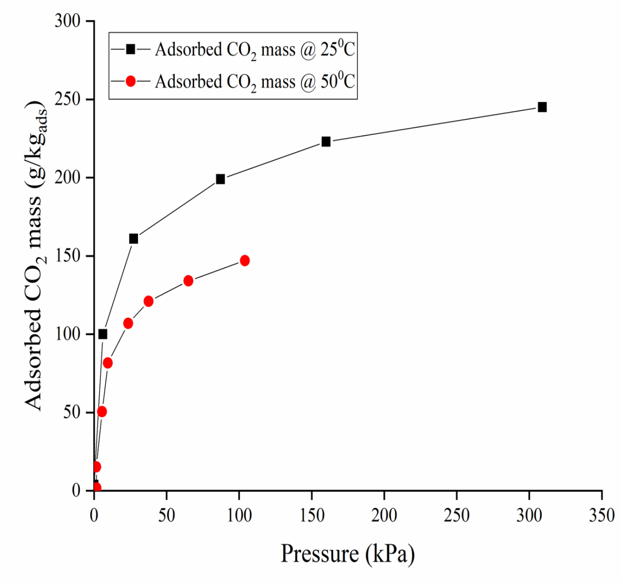

Fig. 2. Adsorbed CO_2 mass in Zirconia 13X with respect to temperature and pressure

2. Experimental Setup and Test Procedure

The experimental setup is shown in Fig.3 and the Kirloskar test engine specification is given in Table 1. The engine is coupled with an eddy current dynamometer for loading purposes. The emission characteristics of the engine is studied by varying the load in five steps from zero to full load condition. Initially, the engine is warmed up for 10 minutes and the load is increased gradually in steps. The fuel used in this study is conventional fuel available at local fuel stations and the properties were shown in table 2. In this experimental study, commercially available zeolite 13X (100 INR/kg) is directly purchased from the Indian market for investigation. The measured surface properties and elemental compositions of the zeolite 13X are given in table 3. A two-way catalytic converter flanked by reduction cones is modified and used as a zeolite bed-chamber. The length of the zeolite bed chamber is kept constant and the weight of the zeolite kept in bed is measured before and after tests using a weighing scale. Before starting the emission tests the setup was checked for a leak. In this work, a quantified amount of zeolite 13X was chosen in three different masses and it is used as a molecular sieve to analyse the CO_2 capturing. The physical structure of the sieve is shown in Fig.4.

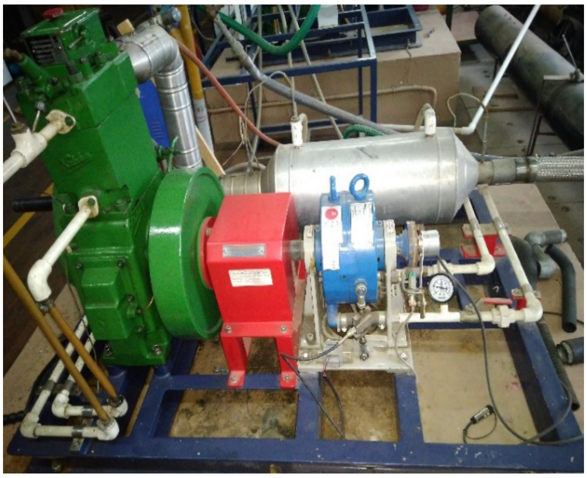

Fig. 3. Experimental layout.

Table 1. Test engine specifications

Parameters	Units	Range
Bore X Stroke	mm	80 X 110
Compression ratio	-	16.5:1
Rated output	kW(hp)	3.7(5) @ 1500 RPM
Torque (full load)	kNm	0.0024
Injection pressure	Bar	220
Injection timing	° bTDC	23

Table 2. Properties of test fuel

Properties	Diesel
Flashpoint	55 °C
Fire point	90 °C
Cetane Number	56
Auto-ignition temperature	254 °C
Calorific value	42500 kJ/kg
Density	840 kg/m^3
Viscosity (@ 20°C)	3.3 centipoises

The study carried out without doing any modifications in the base engine setup is considered as benchmark values and these benchmark values are used to compare with adsorption results. The instrument used for measuring emissions was displayed in table 4.

Fig. 4. Zeolite 13X molecular sieve.

Fig. 5. Zeolite bed chamber.

Table 3. Properties of Zeolite 13X

Parameters	Values	Composition	(wt %)
Shape	Beads dia: 1.6 mm	Sodium	12.2
Particle density	1.25 g/cm^3	Aluminum	13.4
Attrition	0.1 %	Silicon	18.3
Crushing strength	30 N	Calcium	0.5
Water adsorption @ 60 % RH	24.4 %	Potassium	0.2
		Magnesium	1.2

Table 4. Test Instrument

Instrument	Parameter	Measuring Range
AVL Ditest analyzer	NO_x	0 - 20,000 ppm
	HC	0 - 20,000 ppm
	CO	0 - 100%
	CO_2	0 - 100%

3. Results and Discussion

3.1. Carbon dioxide emission

The CO_2 adsorption is observed for five different loads and plotted individually for different zeolite masses. Initially, the engine is tested for thermal efficiency before and after modification and assured for minimum change in efficiency less than a percent as shown in Fig. 6. The adsorption results are recorded maintaining the zeolite bed chamber at 200°C. The amount of CO_2 adsorbed by zeolite 13X is shown in Fig.7. On the overall observation, it is found that 45% of CO_2 emissions were reduced using 200g zeolite molecular sieves compared to 100g and 150g sieves. The exhaust tailpipe is connected to a rectangular chamber to avoid back pressure and is assured for benchmark efficiency. This CO_2 reduction trend also agrees with the Carbon monoxide (CO) reduction and it is evident from the CO emission results as shown in Fig.8. The adsorption range of CO_2 is found similar to the isotherm equations stated above. Similarly, the same trend is followed by oxides of nitrogen emission. Because zeolites are capable to absorb NO emission. The adsorption time for CO_2 active adsorption is shown in table 5. After conducting the experiments, the mass of the bed before desorption weighted and it is found to be increased from the original mass. It proves the adsorption of emissions by the zeolites. The chemical reaction behind the CO_2 adsorption is given in Eq. (4).

$$(\text{metal ion})^{m+} \rightarrow {}^{n-}O{=}C{=}O^{n+} \qquad (4)$$

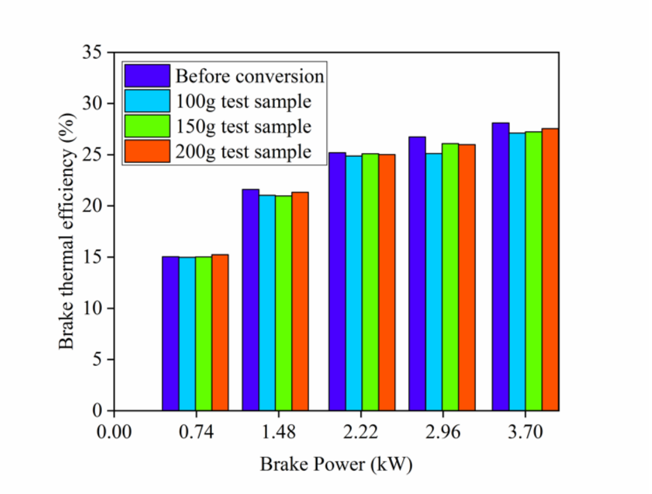

Fig. 6. Brake thermal efficiency vs Engine brake power.

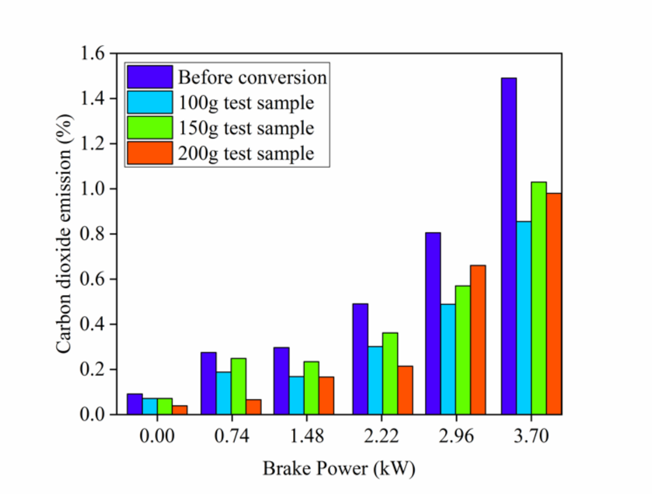

Fig. 7. Carbon dioxide emissions vs Engine brake power.

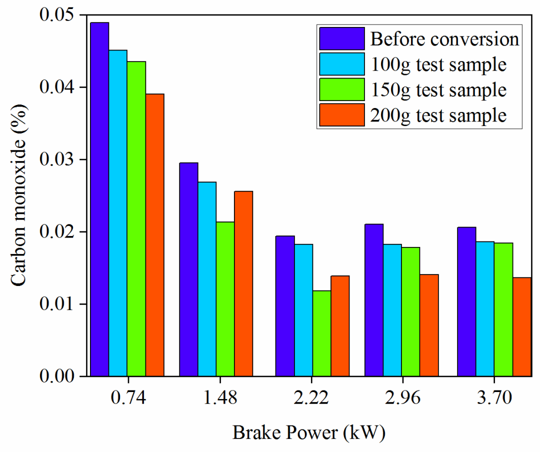

Fig. 8. Carbon monoxide emissions vs Engine brake power.

3.2. Hydrocarbon emission

The amount of unburned hydrocarbon (HC) emission emitted from the engine before and after the zeolite bed is shown in Fig.9. From the Fig.9, it is found that HC emissions decreased at all the loads. Compared to 100g and 150g molecular sieves, the 200g zeolite test sample shows a maximum adsorption ion of HC emissions. However, there is no significant difference between the adsorption quantities in part and medium loads. Zeolites are capable of absorbing CO_2 emissions might also be the reason for reduced CO and HC emissions. The maximum adsorption of HC emissions is found as 26% compared to benchmark results.

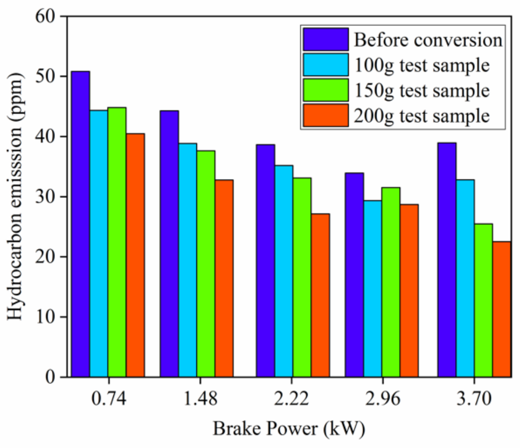

Fig. 9. Hydrocarbon emission vs Engine brake power.

3.3. Oxides of nitrogen emission

Zeolites are capable of adsorbing both CO_2 and NO emissions. The adsorbed NO emission concerning different loads is shown in figure 10. The reduction in exhaust gas temperature passing after the zeolite bed-chamber might also be the reason for NO emission reduction. Overall, 45% of NO_x emissions were adsorbed by molecular sieves. The NO_x capacity of zeolites is less than CO_2 adsorbing capacity. Pressure swing and temperature swing adsorption techniques are used to regenerate the adsorbed CO_2 gas [27, 28]. For desorbing the observed gas emissions, using a heated bed vacuum chamber the adsorbed gas is collected at a vacuum pressure of 0.6 atmospheres. On the other hand, the testbed zeolite samples were soaked into the fresh lime water. The operating temperature is kept at 100 °C [29]. It is observed that fresh white-colored lime water changes to milky which indicates the presence of CO_2 in test zeolites.

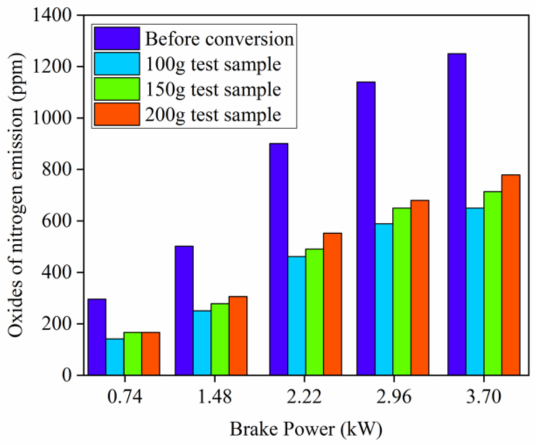

Fig.10. Oxides of nitrogen emission vs Engine brake power.

The presence of CO_2 in the zeolites turns the lime water to milky. Once the test is completed the zeolite beds are connected with a vacuum pump to desorb the CO_2 in one end and another end is closed. The temperature of the zeolite chamber is maintained at 100 °C at 0.6 atmospheres. The initial mass of the zeolites, bed adsorption cycle time, the mass of desorption and restoration percentage are shown in table 5. The end of the vacuum pump is connected to the storage unit where the compressed CO_2 is stored for industrial uses.

Table 5. Restoration analysis

Initial mass of zeolites (g)	Bed adsorption cycle time (minutes)	Mass of bed post desorption (g)	Restoration	
			time (minutes)	(%)
100	30	122	20	95.5
150	60	164.4	34	95.8
200	90	270.5	40	96.3

4. Conclusion

Existing commercial three-way catalysts utilize precious metals so it founds to be non-economic. However, these zeolites are low cost and capable of adsorbing CO_2 and NO_x emissions. Adopting CO_2 adsorption using zeolites is lesser energy consumption and efficient process. Moreover, the adsorbed CO_2 is regenerated and utilized in industries like metal industry, mining industry, welding system, carbonated beverages and fire extinguishers. Thus utilizing the waste CO_2 generated from the engine exhausts tends the society to reduce emissions. The experiment is mainly concentrated on CO_2 and NO_x emissions and the results found to be a significant reduction of these emissions. This technique is also can be implemented for flue gas separation in industries. However, these adsorbed gases can be easily regenerated and further used in small scale industries. This experiment can be extended to various bed lengths of different zeolite masses with various adsorption times. Hence, an optimum mass of zeolite is found out to achieve better economic and limited space conditions. Furthermore, research is appreciated to work on mass reduction of CO_2 emission from the diesel engine operated generators located in domestic places like hospitals, banks and academic institutions. Since the engines are stationary it is mandatory to reduce the CO_2 emissions in those particular locations.

References

[1] W. Kularathne, C. A. Gunathilake, A. C. Rathneweera, C. S. Kalpage, and S. Rajapakse, “The Effect of Use of Biofuels on Environmental Pollution - A Review,” Int. J. Renew. Energy Res., vol. 9, pp. 1355–1367, September 2019.

[2] M. Beken, B. Hangun and O. Eyecioglu, "Classification of Turkey among European Countries by Years in Terms of Energy Efficiency, Total Renewable Energy, Energy Consumption, Greenhouse Gas Emission and Energy Import Dependency by Using Machine Learning," 8th International Conference on Renewable Energy Research and Applications (ICRERA), Brasov, pp. 951-956, 3-6 November 2019.

[3] H. I. Bulbul, M. Colak, A. Colak and S. Bulbul, "Public awareness and education for renewable energy and systems," 6th International Conference on Renewable Energy Research and Applications (ICRERA), San Diego, pp. 12-12, 5-9 November 2017.

[4] O. J. Reátegui et al., "Biogas production in batch in anaerobic conditions using cattle manure enriched with waste from slaughterhouse," 6th International Conference on Renewable Energy Research and Applications (ICRERA), San Diego, pp. 819-822, 5-9 November 2017.

[5] Y. Ulusoy, A. H. Ulukardesler, R. Arslan and Y. Tekin, "Energy and emission benefits of chicken manure biogas production — A case study," 6th International Conference on Renewable Energy Research and Applications (ICRERA), San Diego, pp. 648-652, 5-9 November 2017.

[6] Y. Ulusoy and A. H. Ulukardesler, "Biogas production potential of olive-mill wastes in Turkey," 6th International Conference on Renewable Energy Research and Applications (ICRERA), San Diego, pp. 664-668, 5-9 November 2017.

[7] R. Rajkumar, K. G. Kannan, and M. Mohanraj, “A comparative study of performance and emission characteristics of a diesel engine using various non-edible extracts,” Prog. Ind. Ecol., vol. 14, no. 2, pp. 91–103, September 2020.

[8] D. Yamegueu and S. Sidibe, “Experimental Investigation of the Power Quality of Diesel Engines Operating With Straight Jatropha Curcas Oil,” Int. J. Renew. Energy Res., vol. 9, pp. 1772–1781, December 2019.

[9] R. Nikhom, C. Mueanmas, and K. Suppalakpanya, “Enhancement of Biodiesel Production from Palm Fatty Acid Distillate Using Methyl T-Butyl Ether Co-Solvent: Process Optimization,” Int. J. Renew. Energy Res., vol. 9, pp. 1319–1327, September 2019.

[10] C. Srinidhi and A. Madhusudhan, “A Diesel Engine Performance Investigation Fuelled with Nickel Oxide Nano Fuel-methyl Ester,” Int. J. Renew. Energy Res., vol. 7, pp. 676–681, 2017.

[11] International Energy Agency, “India 2020 Energy Policy Review,” 2020.

[12] P. Planning and A. Cell, “All India Study on Sectoral Demand of Diesel & Petrol,” 2013.

[13] A. Samanta, A. Zhao, G. K. H. Shimizu, P. Sarkar, and R. Gupta, “Post-combustion CO_2 capture using solid sorbents: A review,” Ind. Eng. Chem. Res., vol. 51, pp. 1438–1463, October 2011.

[14] E. I. Koytsoumpa, C. Bergins, and E. Kakaras, “The CO_2 economy: Review of CO_2 capture and reuse technologies,” J. Supercrit. Fluids, vol. 132, pp. 3–16, July 2017.

[15] Q. Wang, J. Luo, Z. Zhong, and A. Borgna, “CO_2 capture by solid adsorbents and their applications: Current status and new trends,” Energy Environ. Sci., vol. 4, no. 1, pp. 42–55, 2011.

[16] L. M. Mulloth and J. E. Finn, “Carbon Dioxide Adsorption on a 5A Zeolite Designed for CO_2 Removal in Spacecraft Cabins,” 1998.

[17] M. B. Pourazar, T. Mohammadi, M. Reza, J. Nasr, and M. Javanbakht, “Preparation of 13X zeolite powder and membrane: investigation of synthesis parameters impacts using experimental design,” Mater. Res. Express, vol. 7, pp. 035004, March 2020.

[18] P. A. P. Mendes, A. M. Ribeiro, K. Gleichmann, A. F. P. Ferreira, and A. E. Rodrigues, “Separation of CO_2/N_2 on binderless 5A zeolite,” J. CO_2 Util., vol. 20, pp. 224–233, June 2017.

[19] J. Merel, M. Clausse, and F. Meunier, “Experimental investigation on CO_2 post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites,” Ind. Eng. Chem. Res., vol. 47, pp. 209–215, 2008.

[20] D. Karthikeyan, “Research on Metal Doped Zeolite as Catalyst to Reduce NO_X Emission from Lean Burn Gasoline Engines,” Int. J. Eng. Adv. Technol., vol. 8, pp. 201–206, July 2019.

[21] S. Cavenati, C. A. Grande, and A. E. Rodrigues, “Adsorption Equilibrium of Methane, Carbon Dioxide,

and Nitrogen on Zeolite 13X at High Pressures," J. Chem. Eng. Data, vol. 49, pp. 1095–1101, 2004.

[22] F. Su, C. Lu, S. C. Kuo, and W. Zeng, "Adsorption of CO2 on amine-functionalized y-type zeolites," Energy and Fuels, vol. 24, pp. 1441–1448, 2010.

[23] M. H. Zarghampoor, M. Mozaffarian, M. Soleimani, and M. Takht Ravanchi, "Modeling of CO_2 Adsorption on Activated Carbon and 13X Zeolite via Vacuum Swing Adsorption," IOP Conf. Ser. Mater. Sci. Eng., vol. 206, 2017.

[24] Z. H. Javed, M. Shabir, and M. Riaz, "Agricultural Productivity and CO_2 Emission in Pakistan: An Econometric Analysis," Int. J. Renew. Energy Res., vol. 8, pp. 1535–43, September 2018.

[25] J. S. Lee, J. H. Kim, J. T. Kim, J. K. Suh, J. M. Lee, and C. H. Lee, "Adsorption equilibria of CO_2 on zeolite 13X and zeolite X/activated carbon composite," J. Chem. Eng. Data, vol. 47, pp. 1237–1242, 2002.

[26] C. Chen, S. S. Kim, W. S. Cho, and W. S. Ahn, "Polyethylenimine-incorporated zeolite 13X with mesoporosity for post-combustion CO_2 capture," Appl. Surf. Sci., vol. 332, pp. 167–171, 2015

[27] M. Wang, A. Lawal, P. Stephenson, J. Sidders, and C. Ramshaw, "Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review," Chem. Eng. Res. Des., vol. 89, pp. 1609–1624, 2011.

[28] R. V Siriwardane, M. Shen, E. P. Fisher, P. O. Box, W. Virginia, and J. Losch, "Adsorption of CO_2 on Zeolites at Moderate Temperatures," Energy and Fuels, vol. 19, pp. 1153–1159, 2005.

[29] L. Joss, M. Gazzani, and M. Mazzotti, "Rational design of temperature swing adsorption cycles for post-combustion CO_2 capture," Chem. Eng. Sci., vol. 158, pp. 381–394, 2017.