

# The use of anaerobically digested slurry combined with natural zeolite for rapeseed production

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## Abstract

The objective of this study carried out at the Solar Energy Institute in Ege University, Izmir, was to investigate utilization of anaerobically digested cattle slurry combined with natural zeolite for rapeseed production. "Bristol" winter rapeseed cultivar was used as plant material in this study and the value of slurry as fertilizer for growing rapeseed was compared with commercial fertilizers. The anaerobically digested slurry may not be a suitable soil improver in its basic form owing to its viscosity. Therefore, further treatment can be essential to enhance its applicability as a crop fertilizer before use as an acceptable saleable product. In this study, natural zeolite as a bulking agent for improving quality of anaerobically digested cattle slurry was also applied to soil and found to have a beneficial effect on the characteristics of the end product. It was obtained positive results on plant growth and yield components of rapeseed by the addition of clinoptilolite to anaerobically digested cattle slurry.

*Keywords:* Animal waste; Anaerobic fermentation; Biogas; Biomass energy; Energy crops; Rapeseed; Canola; Cattle slurry; Digested slurry; Renewable energy; Zeolite; Clinoptilolite

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## 1. Introduction

Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs. The most cost effective means of meeting our energy needs whilst tackling climate change is by using energy more efficiently and utilizing renewable energy. Renewable energy is a prerequisite for achievement sustainable development. Renewable energy can play a crucial role in providing energy access as well as in reducing greenhouse gas emissions, enhancing energy security, and accelerating economic growth and employment. Renewable energy sources such as biomass, wind, solar, hydropower, and geothermal can provide sustainable energy services, based on the use of routinely available, indigenous resources.

Biomass has become one of the most commonly used renewable sources of energy in the last two decades. Biomass has been used for heating and cooking for thousands of years. With today's technology, plant materials can be used to generate electricity, heat, or liquid fuels for motor vehicles that have substantially lower environmental impacts than traditional fossil fuels. Biomass energy goes into division as classic and modern. As modern biomass energy technologies, energy forestry and energy crops production can be counted. To apply modern biomass energy technology, energy crops

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production, planning of energy and planning of agrarian production have to be considered together [1]. As modern biofuels, bioethanol, biogas, biodiesel, gases obtained from gasification, products of pyrolyses, biomethanol, biohydrogen, etc. can be counted. All these kind of biomass energy can be used for agricultural activities. But also, they firstly have to grow up. So, using biomass energy in agriculture and biomass resources production are related with each other [2].

Biogas technology can not only provide fuel, but is also important for comprehensive utilization of biomass forestry, animal husbandry, fishery, agricultural economy, protecting the environment, realizing agricultural recycling, as well as improving the sanitary conditions, in rural areas [3]. Anaerobic digestion of animal manure has the general goal of convert organic residues into two categories of valuable products: on one hand biogas, a renewable fuel further used to produce green electricity, heat or as vehicle fuel and on the other hand the digested substrate, commonly named digestate, and used as fertilizer in agriculture. Digestate can as well be further refined into concentrated fertilizers, fiber products and clean water, all suitable for recycling [4].

Biodiesel is another bioenergy kind gained from oleaginous seeds such as canola, safflower and sunflower. Also, used frying oil, fish oil can be chosen. The biggest advantage of using biodiesel is environmentally friendly that it has over gasoline and petroleum diesel, its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content [5], higher cetane number, and higher biodegradability [6]. Also, using biodiesel benefits as economically because of potential amounts and it can reduce import of fuel oil amounts from abroad [2].

Zeolites are a family of crystalline aluminosilicate minerals. The unit structure of zeolite is  $\text{AlO}_4$  or  $\text{SiO}_4$  tetrahedral. These minerals have channels and pores in their initial structures, and these pores have water molecules and changeable cations. Water molecules leave a zeolitic structure by heating easily or can be adsorbed again [7, 8]. As non-toxic, ecologically advantageous and affordable materials, the natural zeolites, due to their structural, ion exchange and sorption properties and also many other characteristics are well suited for agricultural uses in animal as well as plant production. The natural zeolite of the clinoptilolite type is one of the world's most abundantly occurring and most abundantly used zeolitic minerals. At present it is widely used in many fields of industrial technology, agricultural production, ecology, but also in other areas such as medicine, pharmacy [9].

In Turkey, it is very important to develop and demonstrate environmentally acceptable energy crops and cropping systems for producing large quantities of low-cost, high-quality biomass feedstocks. Anaerobic digestion can enrich alternative agricultural practices when the digestion residues are applied to energy crops and other dedicated feedstocks for the production of alternative fuels such as biodiesel or ethanol. Treating commodities to produce another energy yield while recycling nutrients creates a virtuous cycle of sustainability [10].

The objective of this study was to investigate utilization of anaerobically digested slurry combined with natural zeolite for rapeseed production.

## 2. Materials and methods

In this study carried out at the Solar Energy Institute in Ege University, Izmir, the eco-agricultural system was investigated and used anaerobically digested cattle slurry as fertilizer for rapeseed production. Also natural zeolite as a bulking agent for improving quality of anaerobically digested cattle slurry was applied to soil.

### 2.1. Anaerobic digestion system

Description of anaerobic digestion system used in the present study may be summarized as follows:

- Reactor volume: 280 l
- Reactor temperature: 37 °C
- Feeding material: Diluted cattle manure
- Feeding type: Batch
- Total Solid Rate: 9 %
- Heated System: Solar water heater and auxiliary heater
- Mixing system: Hydrolic mixing by open impeller centrifugal pump
- Gas Holder: Water replaced type

The digested slurry discharged from this system was applied as fertilizer to grow rapeseed which would then

be used to produce biodiesel. Elemental composition was determined in order to observed the suitability of anaerobically digested cattle slurry as a crop fertilizer for agricultural land. The elemental analysis results of the initial cattle manure and the digested cattle slurry discharged from this system were given in Table 1.

**Table 1. The elemental analysis of cattle manure and digested cattle slurry**

Organic materials	(%) C	(%) H	(%) N	(%) S
Cattle manure	13.380	9.121	0.365	0.112
Anaerobically digested cattle slurry	4.748	9.284	0.194	0.038

## 2. 2. Rapeseed (*Brassica napus ssp. oleifera* L.) production

The field study was carried out in irrigated conditions at the experiment area of the Solar Energy Institute in Izmir (latitude 38.24 °N, longitude 27.50 °E), Turkey, in 2004-2005. Mean temperature of experiment area was measured as 14 °C during growing period between October 20<sup>th</sup> and May 20<sup>th</sup>. The lowest average temperature was 6 °C and the highest was recorded as 26 °C. Relative humidity (%) was determined to be 65. Some soil properties related to research location are summarized in Table 2.

**Table 2. Some physical and chemical properties of soil in the experiment area**

pH	7.200
Total salt (%)	0.075
Lime (%)	6.900
Sand (%)	64.040
Silt (%)	17.960
Clay (%)	18.000
Structure	Loamy
Organic Matter (%)	3.612
Total Nitrogen (%)	0.140
Available Phosphorus (Ppm)	0.810
Available Potassium (Ppm)	361.000
Available Calcium (Ppm)	4500.000
Available Magnesium (Ppm)	150.000
Available Sodium (Ppm)	24.300
Available Iron (Ppm)	88.320
Available Copper (Ppm)	13.590
Available Zinc (Ppm)	36.720

As shown in Table 2, soil has a neutral reaction type. There is no risk in terms of total soluble salt. A Lime-rich soil sample has a loam structure. Humus is in mid-sufficient amount and total nitrogen is fine. Phosphorus is one macronutrient which can be taken by the plant is in poor conditions, although other macronutrients are sufficient. Also available micronutrient amounts are sufficient.

Rapeseed (*Brassica napus*), also known as canola, is a bright yellow flowering member of the family Brassicaceae. Canola is one of two cultivars of rapeseed or *Brassica compestris*. The plant germinates quickly, forming a deep growing taproot and a rosette of blue-green leaves from which emerge 7–10 lateral shoots. On the ends of the branched stems grow the gold-yellow flowered racemes. Each plant has approximately 120 long slender seed pods; 40 to 60 of these are found on the main shoot. Each seed pod contains 18–20 seeds (2000–3000 seeds per plant) [11, 12]. The seeds are small, round and black. Rapeseed is an important annual oilseed crop whose oil is the most commonly used in biodiesel production. Rapeseed has both winter and spring forms [12].

“Bristol” winter rapeseed cultivar was used as plant material in this study. Organic fertilization using liquid manure is possible and recommended on rapeseed production. Nitrogen fertilizer should be used according to the development of the crop. Nitrogen is an essential plant nutrient, but is also an important input increase the cost of the its production. Therefore, the determination of the most suitable fertilizer will both increase the yield and decrease the cost. In the present study, the value of slurry as fertilizer for growing rapeseed was compared with commercial fertilizers. Anaerobically digested cattle slurry has significant potential as a crop fertilizer and soil conditioner [10]. On the other hand, this slurry may not be a suitable soil improver in its basic form owing to its viscosity. Therefore, further treatment can be essential to enhance its applicability as a crop fertilizer before use as an acceptable saleable product. For this reason, natural zeolite as a bulking agent for improving quality of anaerobically digested cattle slurry was also applied to soil in this experiment. Clinoptilolite type of natural zeolite, which is also the most important minerals over the World was used in the experiment. The natural clinoptilolite mined in Gordes was supplied from Gordes Mining Corporation, Izmir, Turkey. Gordes clinoptilolites have a high-purity mineral quality and are homogeneous with mine reserve of one billion tons [8]. The particle sizes of this clinoptilolite were between 1.8 and 3.5 mm. Mineralogical, chemical and physical properties of

Gordes clinoptilolite are given in Table 3. Clinoptilolite dose of 10 % was applied based on the mass of soil found 1 m<sup>3</sup>.

According to this, 6 treatment used in this study may be given as follows:

- Anaerobically digested cattle slurry (ADCS)
- Anaerobically digested cattle slurry and clinoptilolite (ADCS + C)
- Compose fertilizer as chemical fertilizer (15-15-15) (CF)
- Compose fertilizer as chemical fertilizer (15-15-15) and clinoptilolite (CF + C)
- Clinoptilolite (C)
- Control (non-fertilized control) (NFC)

**Table 3. Mineralogical, chemical, and physical properties of Gordes Clinoptilolite [8]**

Mineralogical content (%)	
Clinoptilolite	85–98
Feldspar	0–10
Clay, mica, etc.	0–15
Chemical composition (%)	
SiO <sub>2</sub>	70.90
Al <sub>2</sub> O <sub>3</sub>	12.40
Fe <sub>2</sub> O <sub>3</sub>	1.21
K <sub>2</sub> O	4.46
MgO	0.83
Na <sub>2</sub> O	0.28
CaO	2.54
TiO <sub>2</sub>	0.089
MnO	<0.01
P <sub>2</sub> O <sub>5</sub>	0.02
Lost of ignition (LOI)	7.20
Some physical properties	
Bulk density	500–1,200 g/cm <sup>3</sup>
Specific gravity	1,800–2,250 g/cm <sup>3</sup>
Apparent porosity	39.4–44.2 %
Thermal stability	Up to 750 °C
Blain, surface area value	40.79 m <sup>2</sup> /g
Cation Exchange capacity	1.2–2.2 meq/g

Each form of fertilizer was applied to provide the equivalent of 14 kg N/ha pure nitrogen at the recommended doses for rapeseed production on the basis of soil test [13].

The experimental plots were approximately 1.05 m<sup>2</sup> (1 x 1.05 m), each with 40 rapeseed plants. According to these treatments, the fertilizers used in this experiment were applied, before sowing, to the soil. The seeds were sown on 20<sup>th</sup> October 2004, at a recommended spacing of 25 by 15 cm in plots 1 x 1,05 m in size. The harvesting was carried out on 20<sup>th</sup> May 2005 by hand.

The present study was planned according to the completely randomized block design with three replicates. Anaerobically digested cattle slurry, anaerobically digested cattle slurry and clinoptilolite, compose fertilizer (15-15-15), compose fertilizer (15-15-15) and clinoptilolite, clinoptilolite were compared to the non fertilized control and their effects on plant growth and yield components of safflower were investigated. During the growing season data collection was performed on the number of plant per plot, plant height (cm), plant diameter (cm), the number of lateral branches on the main stem, the number of pods per plant, the number of seed per pod, total seed yield (kg da<sup>-1</sup>) and thousand seed weight. In addition to these, the elemental composition of the crop residues of rapeseed and some physical, chemical properties of the soil after harvest of the crop in the experiment area were analyzed according to treatments. The collected data were subjected to analysis of variance, and treatments were compared with the least significant difference (LSD) test and orthogonal comparisons.

### 3. Results and discussion

Effects of the treatments on some physical, chemical properties of the soil after harvest of the crop in the experiment area are presented in Table 4. In addition to these, the elemental composition data of the crop residues of rapeseed after harvest according to treatments are given in Table 5.

The effects of the treatments on plant growth and yield components of rapeseed were found statistically significant (99 %) (Table 6). As shown in Table 6, the plant number, plant height and diameter of plant were increased by all applications according to control. Especially, these plant growth parameters were significantly higher in the application of anaerobically digested cattle slurry and clinoptilolite compared to other treatments (Fig 1). The rapeseed plants grown in the plots applied

**Table 4. Effects of the treatments on some physical and chemical properties of soil in the experiment area**

	ADCS	ADCS + C	CF	CF + C	C	NFC
pH	7.940	7.990	8.050	8.000	8.050	7.940
Total salt (%)	0.065	0.052	0.062	0.084	0.089	0.089
Lime (%)	14.800	14.800	16.200	14.300	13.200	16.100
Sand (%)	61.280	65.280	67.280	67.280	65.280	59.280
Silt (%)	24.720	20.720	20.720	18.720	18.720	24.720
Clay (%)	14.000	14.000	12.000	14.000	16.000	16.000
Structure	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam
Organic Matter (%)	2.600	2.500	1.900	1.400	1.700	2.100
Total Nitrogen (%)	0.119	0.108	0.108	0.101	0.102	0.110
Available Phosphorus (Ppm)	1.500	1.400	1.100	1.300	1.200	1.000
Available Potassium (Ppm)	280	290	240	260	300	310
Available Calcium (Ppm)	3200	2900	3400	2900	3200	3100
Available Magnesium (Ppm)	282	268	267	268	329	227
Available Sodium (Ppm)	110	90	100	120	110	100
Available Iron (Ppm)	24	20	17	19	18	21
Available Copper (Ppm)	1.200	0.850	0.850	1.000	0.910	1.200
Available Zinc (Ppm)	47	39	21	21	25	19
Available Manganese (Ppm)	21	27	25	28	36	33

**Table 5. Elemental composition of the crop residues of rapeseed after harvest according to treatments**

Treatments	(%) C	(%) H	(%) N	(%) S
Anaerobically digested cattle slurry and clinoptilolite	40.19	5.900	0.564	0.322
Anaerobically digested cattle slurry	39.66	5.826	0.898	0.468
Compose fertilizer (15-15-15) and clinoptilolite	42.07	6.045	0.694	0.279
Compose fertilizer (15-15-15)	40.36	5.937	0.566	0.368
Clinoptilolite	40.37	5.917	0.544	0.200
Control (non-fertilized control)	39.54	5.785	0.456	0.372

with anaerobically digested cattle slurry and clinoptilolite had the highest plant height and the widest diameter on 20<sup>th</sup> May (the harvesting date). Contrary, the plants grown in the non fertilized control plots had the shortest plant height and the narrowest diameter. As it can be seen from Fig. 2 and Fig. 3, while the highest plant height and the widest diameter were obtained from the application of anaerobically digested cattle slurry and clinoptilolite as 126.13 cm and 1.41 cm, respectively, the control plants had the shortest plant height as 83.97 and the narrowest plant diameter as 0.90 cm at the harvesting date. Other treatments were ranked as: anaerobically digested cattle fertilizer > compose fertilizer and clinoptilolite > compose fertilizer > clinoptilolite for the plant height and diameter. However, it can still be said that the number of lateral branches on the main stem was significantly increased by all fertilizers and better with anaerobically digested cattle slurry and clinoptilolite than with the other treatments.

**Table 6. Effects of the treatments on plant growth and yield components of rapeseed**

Treatments	Plant number	Plant height (cm)	The diameter of plant (cm)	The number of lateral branches	The number of pods per plant	The number of seed per pod	Total seed yield (kg da <sup>-1</sup> )	Thousand seed weight
Anaerobically digested cattle slurry and clinoptilolite	38.33 a	126.13 a	1.41 a	8.40 a	312.20 a	27.47 a	480.20 a	2.82 a
Anaerobically digested cattle slurry	35.67 ab	123.73 a	1.31 a	7.27 ab	274.60 a	27.40 a	375.53 ab	3.00 a
Compose fertilizer (15-15-15) and clinoptilolite	33.33 ab	116.93 a	1.26 ab	6.80 bc	226.20 ab	25.40 ab	366.67 ab	2.86 a
Compose fertilizer (15-15-15)	31.33 ab	105.87 ab	1.08 b	5.73 cd	172.93 bc	21.13 ab	222.87 bc	2.94 a
Clinoptilolite	31.00 ab	85.20 b	1.02 bc	5.73 cd	169.00 bc	20.93 b	193.73 bc	2.61 a
Control (non-fertilized control)	29.33 b	83.97 b	0.90 c	4.67 d	107.33 c	20.33 b	117.47 c	2.66 a
LSD	8.66 **	35.99 **	0.22 **	1.47 **	94.43 **	6.46 **	189.41 **	0.86 **

(\*\*): Indicates significance at the 99 % level of probability  
 Values followed by the same letter(s) are not significantly different at the 99 % level of probability, according to variance analysis.

The application of nitrogenous fertilizer increases the vegetative growth in plants. Many researchers have also reported positive results in plant height with the increasing doses of nitrogenous [10, 14, 15]. Under the light of previous studies [16], it can be said that during fermentation, the NH<sub>4</sub><sup>+</sup> content and pH of the biogas slurry increase, while the dry matter content, C/N ratio, and odor decrease in comparison to animal manures used as organic sources. A reduction of NH<sub>4</sub><sup>+</sup> losses may be

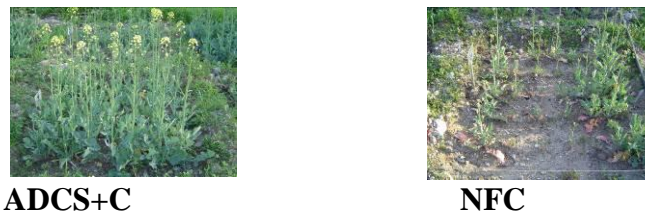


Fig. 1. Differences between the treatments in respect to the plant growth.

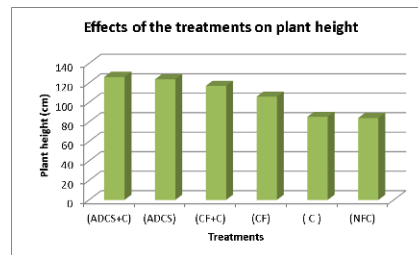


Fig. 2. Changes in plant height with the treatments.

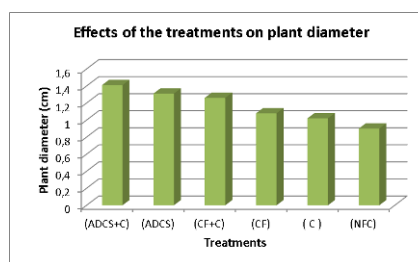


Fig. 3. Changes in plant diameter with the treatments.

expected from the decreased dry matter content and an increased infiltration rate into the soil under good application conditions, but the increase in  $\text{NH}_4^+$  content and pH may have the opposite effect. Consequently, better plant growth parameters have been observed in some cases after biogas slurry application compared to control treatments and unfermented substrates, but not always.

The number of pods per plant and the number of seed per pod were increased by all treatments. As shown in Table 6, the number of pods per plant and the number of seed per pod were significantly higher in the application of anaerobically digested cattle slurry and clinoptilolite compared to other treatments. While the highest number of pods per plant was obtained from the rapeseed plants grown in the plots applied with anaerobically digested cattle slurry and clinoptilolite as 312.20, the control plants had the lowest number of pods per plant as 107.33. Similarly, it can be also seen in Fig. 4, the plants grown in the plots applied with anaerobically digested cattle slurry and clinoptilolite gave the highest seed yield with  $480.20 \text{ kg da}^{-1}$ . Contrary, the control plants had the lowest seed yield as  $117.47 \text{ kg da}^{-1}$ . Other treatments were ranked as: anaerobically digested cattle fertilizer > compose fertilizer and clinoptilolite > compose fertilizer > clinoptilolite for seed yield.

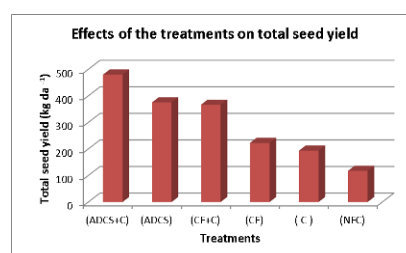


Fig. 4. Changes in the total seed yield with the treatments.

According to these findings, higher yields were obtained from the application of anaerobically digested cattle slurry as fertilizer than the application of compost fertilizer. Also, the addition of natural zeolite to anaerobically digested cattle slurry was found to have a beneficial effect on the characteristics of the end product.

Based on these results, it can be said that anaerobically digested cattle slurry become more effective than others because plant uptake it much more easily and quickly than others. These results obtained are supported by the findings of many researchers [10, 17-23]. Thus, it has determined that crop yields were generally acknowledged to be higher following fertilization with digested slurry. One study using data from the People's Republic of China reported 6 % - 20 % greater yields using digester effluent to meet crop nutrient requirements [19]. It was reported positive results in most vegetable crops such as potatoes, radishes, carrots, cabbage, onions, garlic, etc., And many types of fruit (oranges, apples, guavas, mangos, etc.), sugar cane, rice and jute with slurry fertilization. In contrast, crops such as wheat, oilseed, cotton and baccara reacted less favorably. Slurry is a good fertilizer for pastures and meadows. The available data vary widely, because the fertilizing effect is not only plant-specific, but also dependent on the climate and type of soil [23].

Consequently, recycling of wastes improves soil texture, and thereby decreases input of chemical fertilizers. Also in this study, it was compared the fertilizer value of anaerobically digested cattle slurry with those of chemical fertilizer. Higher yields of rapeseed were obtained with anaerobically digested cattle slurry than compost fertilizer. In previous report of Kocar [10], it was also indicated the input of chemical fertilizers should decrease with the use of anaerobically digested cattle slurry, whereas soil texture is improved.

However, the results of this study showed that the addition of clinoptilolite to anaerobically digested cattle slurry has a beneficial effect on plant growth and yield components of rapeseed. This effect may be attributed to increase in the uptake of some nutrients since zeolite has high cation exchange properties, and acts as a reservoir, holding elements in its structure for slow release to the rhizosphere. The results obtained from this study indicated that natural zeolite could provide economy in nutrient usage and reduce environmental pollution by decreasing the amount of leaching elements. These results are in accordance with the findings of previous studies [24-28]. As reviewed by Arthurson [29], the biogas residue may not be a suitable soil improver in its basic form, owing to possible phytotoxicity, viscosity and odor, difficult handling, and expensive soil application approaches. Therefore, further treatment is essential to enhance its applicability as a crop fertilizer before use as an acceptable saleable product, such as composting (i.e., aerobic degradation) and/or air-drying. In this study, it was determined that the addition of natural zeolite played a very important role to further improve the quality of the anaerobically digested cattle slurry.

#### 4. Conclusions

A good waste management system should be installed throughout the countries where biomass waste potential is available for the optimum use of these wastes in order to minimize the losses and thereby to increase the efficiency. Anaerobic digestion may imply environmental benefits with regard to waste treatment, pollution reduction, energy production, and improvements in agricultural practices [20, 30-33]. As known, the digester supplies biogas as domestic fuel and sludge as fertilizer. Recycling of wastes improves soil texture, and thereby decreases input of chemical fertilizers. The anaerobically digested slurry will not be used and recycled unless farmers accept this product. To convince doubtful farmers and the general public, the value of the anaerobically digested slurry as crop fertilizer and soil conditioner needs to be further confirmed, emphasizing the urgent need for more extensive studies in this field [29].

The anaerobically digested slurry may not be a suitable soil improver in its basic form owing to its viscosity. Therefore, further treatment can be essential to enhance its applicability as a crop fertilizer before use as an acceptable saleable product. In this study, natural zeolite as a bulking agent for improving quality of anaerobically digested cattle slurry was also applied to soil and found to have a beneficial effect on the characteristics of the end product. It was obtained positive results on plant growth and yield components of rapeseed by the addition of clinoptilolite to anaerobically digested cattle slurry.

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