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Transesterification of *Annona squamosa* (Custard apple) seed oil using montmorilloniteK-10 as catalyst and characterization of the fatty acid methyl ester

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Abstract
Organic transformations using environmentally benign catalysts are always getting enormous attention from the chemists. An important family of catalysts that has received considerable attention of the synthetic chemist in recent times is derived from the soil, the most noteworthy ones being clays and zeolites. In this study MontmorilloniteK-10 clay has been used as catalyst for transesterification of *Annona squamosa* (Custard apple) seed Oil. The synthesized product has been characterized by FT-IR, NMR and GC-MS to experiment the viability of the oil as an alternative source of biodiesel.

Keywords: MontmorilloniteK-10, transesterification, *Annona squamosa,* bio-diesel

1. Introduction
Annona squamosa (Sugar apple, Custard apple, and sweetsop) is a common non expensive edible fruit grown in the North-Eastern region of India. *Annona squamosa* is a small well branched tree or shrub of family *Annonaceae* grow abundantly in Assam and North Eastern states of India as the soil here is suitable for these types of fruits. The fleshy part of the fruits can be consumed and the seeds, which contain 27-29% oil average (dry weight basis), are normally thrown away.
Again Montmorillonite clays have been used as catalysts for number of organic reactions and offer several advantages over classical acids. For example the strong acidity, non-corrosive properties, cheapness, mild reaction conditions, high yields and selectivity and the ease of setting and working-up (N Kaur, 2012) [1]. The reactions catalyzed by Montmorillonite are usually carried out under mild conditions with high yields and high selectivity, and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused (Nagendrappa, 2011) [2].

2. Materials and Methods
In this present work, the *Annona squamosa* seed oil, a non-edible oil (Murugesan A 2009) [11] is extracted by using Iodine flask with magnetic stirrer. The seeds were sundried before crushed into powder using grinder. The powdered seeds were placed into the flask and 100ml solvent (Petroleum ether) added and stirred for 5hrs continuously. The oil part was separated from the organic solvent by distillation. Yield was calculated on dry weight basis (Deka DC 2011) [3].

Table 1: Experimental details

Name of seed	*Annona squamosa*
Weight of the powdered seed taken	29.558gm
Solvent taken	100ml
Stirring time	5hrs
Weight of crude oil	8.79gm
Weight of oil after purification	8.532gm
Yield	28.86%

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2.1 Transesterification of *Annona squamosa* oil

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. The homogeneous catalysts include alkalis and acids. The most commonly used alkali catalysts are sodium hydroxide, sodium methoxide and potassium hydroxide. Sulphuric acid, hydrochloric acid and sulfonic acid are usually preferred as acid catalysts. Nowadays, most of the commercial biodiesel comes from the transesterification of vegetable oil using a basic catalyst, such as NaOH, KOH and NaOME, because a basic catalyst can catalyze faster than an acid catalyst (Demirbas A, 2008) [10].
However, homogeneous catalysts have many disadvantages as these lead to reduced yield of biodiesel. Hydrolysis and saponification are side reactions of transesterification resulting in the formation of soap.Soap formations are undesirable side-reactions, because they partially consume the catalyst, decrease the biodiesel yield and complicate the separation and purification steps. Moreover, a large amount of wastewater is produced in separating and cleaning the catalyst and the products. (Jitputti J, 2006) [4].
In this study transesterification of the seed oil was carried out on MontmorilloniteK-10 as catalyst in a round bottom flask with methanol and oil in 10:1 ratio. The reaction was continued approximately at 60 ^{0}C and completion of the reaction was monitored by TLC**.** By the end of the experiment the reaction mixture was transferred into a separating funnel, allowing glycerol to separate by gravity separation (Berrios M 2008) [16]. The product mixture was partitioned between water and petroleum ether and the process of addition and collection of petroleum ether were repeated for at least three times. Upper layer of light petrol containing crude biodiesel collected in a special container before evaporating the solvent. The solvent recovered under vacuum using Buchi make rotavapour. The product was purified by column chromatography over silica gel (60- 120 mesh) using a mixture of petroleum ether and ethyl acetate (25:1) as the eluent. The excess methanol from the bottom layer was removed by rotary evaporator at 90^{0}C and recovered for further use (Atadashi IM, 2011) [13]; (Liu Y 2012) [14]; (Zlatica J 2008) [15].

2.2 Study of the physicochemical properties of the methyl ester of *Annona squamosa*) seed oil (ASME)

The physicochemical parameters of methyl ester of *Annona squamosa*) seed oil (Table-III) was determined to evaluate its potential for use as a feedstock in biodiesel production (Monteiro MR, 2008) [6]; (Knoth G, 2001) [7].
.All the parameters of the FAME involved, like iodine value, saponification value etc. were determined by the standard AOCS (American Oil Chemists Society) methods (ASTM, 2014) [5].

Table 2: Variation of ASME (Annona squamosa Methyl Ester) yield with varying amount of MontmorilloniteK-10

Amount of Mont(% w/w of oil)	1	1.5	2	2.5	**3**	3.5
ASME yield %	69	72	79	85	**89**	89

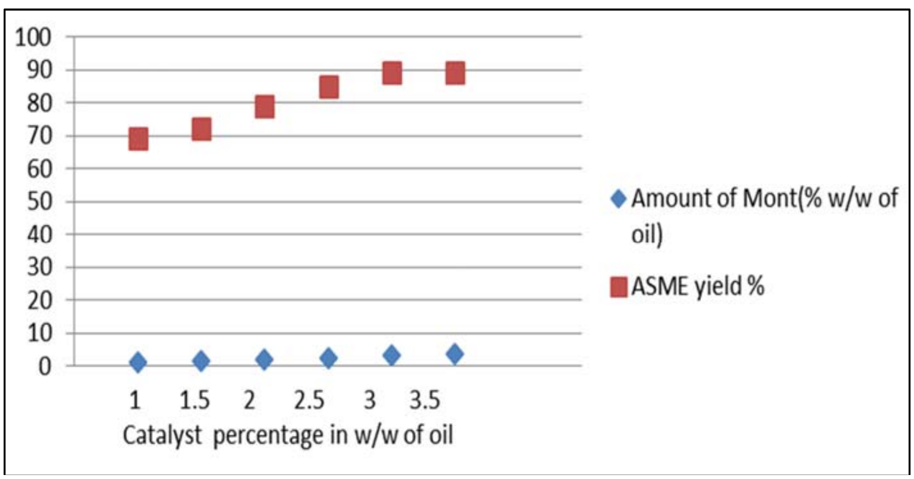

Fig 1: Methyl Ester formation from *Annona squamosa* seed oil using varying amount of MontmorilloniteK-10 as catalyst

Table 3: Properties of FAME of (*Annona squamosa*) seed oil (ASME)

Properties	FAME	EN14214 limits
Kinematic viscosity * (30^{0}C) mm^{2}s^{-1}	3.8	3.5 – 5.0
Sp. Gravity (30^{0}C)	0.821	0.860 -0.900
Saponification number (mg/g)	190	-----
Iodine value (mg iodine/gm)	110	120 max
Cetane Number	48	51min
Acid value, KOH (mg/g) **	0.27	0.5max

* (Babagana G 2012)[8]; ** (Lubrizol, 2013)[9]

3. Result and Discussion

3.1 Characterization of *Annona squamosa* FAME

3.1a ^{1}H NMR (CDCl$_3$, 300MHz): The ^{1}H NMR (CDCl$_3$, 300MHz) spectra (Fig: 2) of the FAME of *Annona squamosa* oil were found to show the following signals-
δ5.29 − 5.33(m) olefinic protons; 3.63 (s) methoxy protons; 2.72−2.76 (t) bis-allylic protons; 2.24-2.39 (t) α-methylene to ester; 1.97-2.03(m) α-methylene to double bond; 1.57-1.61(m) β-methylene to ester; 1.23 - 1.28 (m) backbone methylenes; 0.85 -0.88 (m) terminal methyl protons.

3.1b IR of *Annona squamosa* FAME: Infra-red spectrum (Fig: 3) shows the characteristic absorption at 721.37 due to ν = C – H def; the absorption at 1163.64 due to ν C – O str ; 1654.07 for ν C = C str of unsaturated fatty acids; 1737.2 due to ν C = O str of ester and the band at 2927.96 indicates ν C – H str of – CH_2 –.

3.1c ^{13}C NMR of *Annona squamosa* FAME (Fig:4**):** The singlet (a) is for carbonyl carbon, doublet (b) for olefinic carbons, singlet (**c**) is due to methoxy carbon and the multiplet (d) indicates methylene and methyl carbons.

3.1d GC-MS of *Annona squamosa* FAME (Fig: 5**):** Fatty acid composition of *Annona squamosa* was analyzed by using Perkin Elmer Clarus 600 GC-MS. The individual peaks of the gas chromatogram were analyzed and fatty acids were identified using mass spectra database. Relative percentage of fatty acid esters was calculated from total ion chromatography by computerized integrator. The percentage compositions are shown in Table –IV.

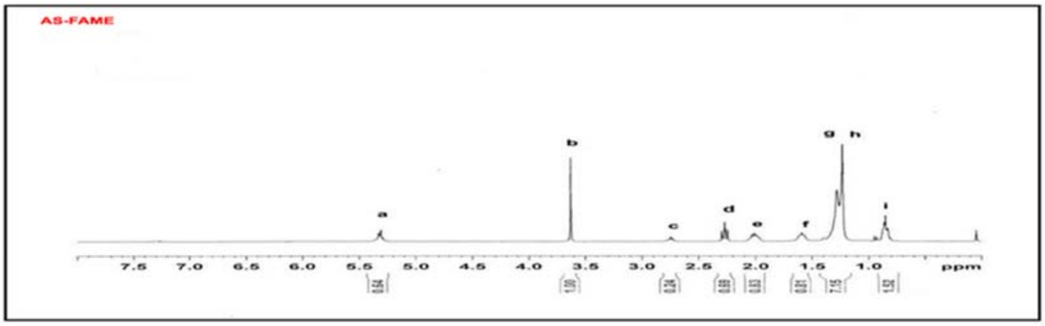

Fig 2: ^{1}H NMR ($CDCl_3$, 300MHz) of *Annona squamosa* FAME

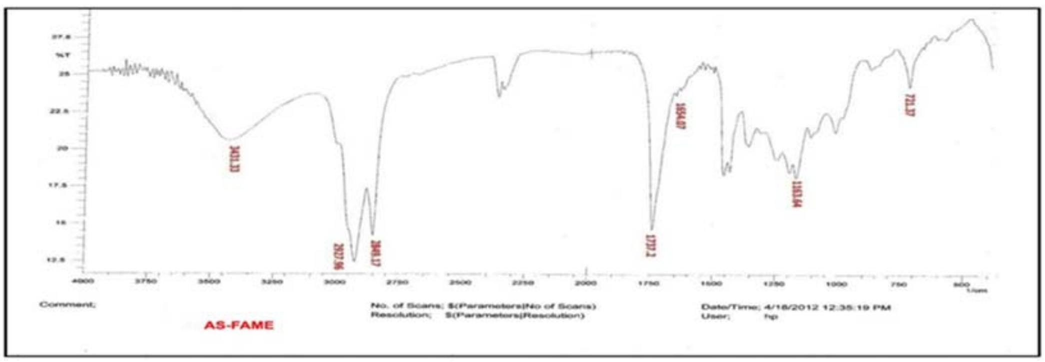

Fig 3: IR (KBr) of *Annona squamosa* FAME

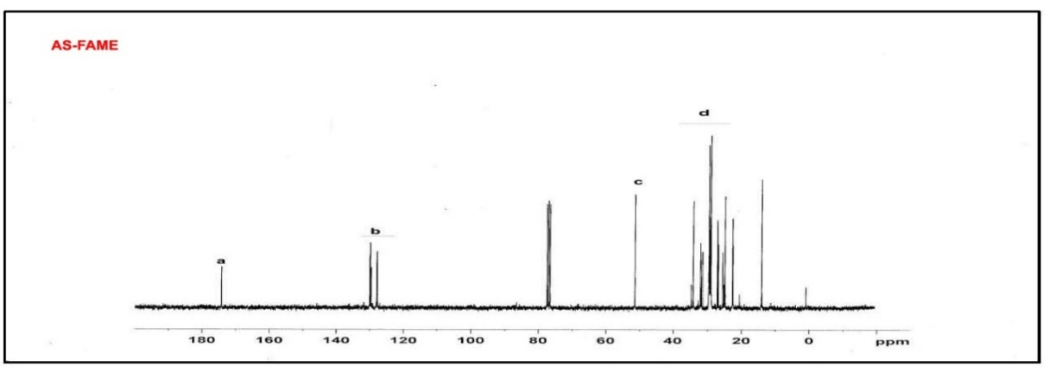

Fig 4: ^{13}C NMR of *Annona squamosa* FAME

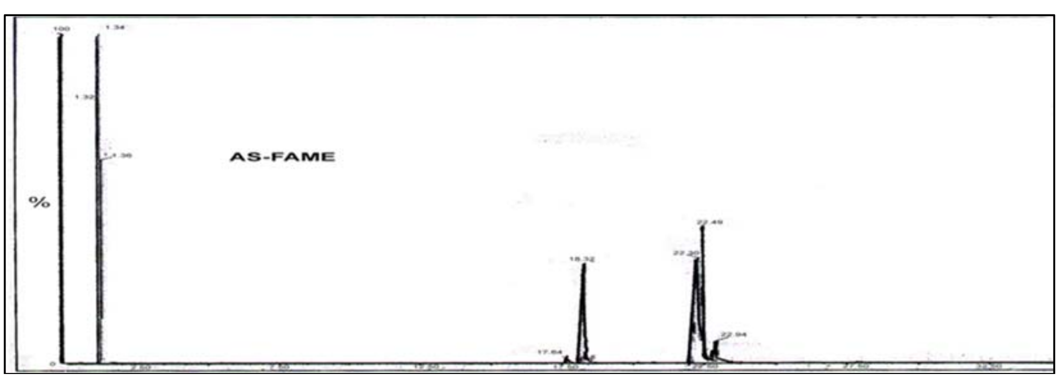

Fig 5: GC of *Annona squamosa* FAME

Table 4: Fatty acids compositions of methyl ester of *Annona squamosa* oil

Retention time (min)	FAME	C to double bond Ratio	%Wt
17.64	Methyl palmitolate	(16:1)	1.2
18.31	Methyl palmitate	(16:0)	28.8
22.30	Methyl linoleate	(18:2)	31.9
22.49	Methyl oleate	(18:1)	33.5
22.94	Methyl stearate	(18:0)	4.6

3.2 Discussion
In this study the amount of oil content from *Annona squamosa* seed was found to be satisfactory (28.86 %). The iodine value and cetane number of the FAME were also found to be within the permissible range. The degree of unsaturation, expressed in terms of the iodine value, is another criterion for selection of biodiesel. Presence of little unsaturated fatty acid component in methyl ester is desirable as it restricts the FAME from solidification to some extent.

Cetane number is the ability of fuel to ignite quickly after being injected. Higher the cetane number is, better is the ignition quality of fuel. Biodiesel standards of USA (ASTM D6751), Germany (DIN 51606) and European Organization (EN 14214) have set this as 47, 49 and 51 respectively. The methyl ester obtained from *Annona squamosa* seed oil meets this specification.

GC-MS analysis shows that the FAME obtained from *Annona squamosa* seed oil is free of soap and the triglycerides are mostly converted to the methyl esters. The fatty acid composition of the methyl esters showed that it is primarily composed of oleic acid, linoleic acid, and palmitic acid.

4 Conclusions
1. Transesterification of *Annona squamosa* seed oil can be carried out using MontmorilloniteK-10 clay as catalyst and possibility of soap formation during the reaction is completely avoidable.
2. The catalyst can be recovered and reuse for further reaction by thorough washing with methanol.
3. The *Annona squamosa* seed contains good amount of oil 27-29% and biodiesel can be produced from *Annona squamosa* seeds oil.
4. The ester formation takes place at room temperature taking 3% MontmorilloniteK-10 (by the weight of the oil) at atmospheric pressure for 2 h reaction time.
5. All of the parameters determined for the methyl ester of *Annona squamosa* seed oil comply with the European FAME standard EN14214.

5 Acknowledgement
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6. References

1. Kaur N, Kishore D. Montmorillonite: An efficient, heterogenous and green catalyst for organic synthesis, JOCPR. 2012; 4(2):991-1015.
2. Nagendrappa Gopalpur. Organic synthesis using clay and clay supported catalysts, Applied Clay Science. 2011; 53:106-138.
3. Deka DC, Basumatary S. High quality biodiesel from yellow oleander (*Thevetiaperuviana*) seed oil. *Biomass and Bioenergy*. 2011; 35:1797-1803.
4. Jitputti J, Kitiyanan B, Rangsunvigi P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem Eng J. 2006; 116:61-66.
5. Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuel. ASTM International, www.astm.org/Standards/D6751.htm (2014)
6. Monteiro MR, Ambrozin AP, Lião LM, Ferreira AG. Critical review on analytical methods for biodiesel characterization. *Tolanta*. 2008; 77:593-605.
7. Knoth G. Analytical methods used in the production and fuel quality assessment of Biodiesel. *Trans ASAE*. 2001; 44:193-200.
8. Babagana G, Bamidele SS, Bugaje IM. Biodiesel kinematic viscosity analysis of *Balanite aegyptiaca* seed oil. ARPN Journal of Engineering and Applied Science. 2012; 7:432-435.
9. Lubrizol. Determination of acid value and free fatty acid. Procdure, Lubrizol test, 2013.
10. Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy conversion and Management*. 2008; 49:125-130.
11. Murugesan A, Umarani C, Chinnusamy TR, Krishnan M, Subramanian R. Production and analysis of biodiesel from non-edible oils- A review. Renewable and Sustainable Energy Reviews. 2009; 13:825-834.
12. Serio MD, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind Eng Chem Res. 2006; 45:3009-3014.
13. Atadashi IM, Aroua MK, Aziz AA. Biodiesel separation and purification: A review. Renewable Energy. 2011; 36:437-43.
14. Liu Y, Chen Y, Yi HF, Wu YL, Yang MD, Chen Z, Tong JM. Column chromatography purification and analysis of biodiesel by transesterification."Guang Pu Xue Yu Guang Pu Fen Xi." [jour] Pub Med 2012; 32(2):505-09.
15. Zlatica J. Predojević. The production of biodiesel from waste frying oils: A comparison of different purification steps. Fuel 2008; 87(17-8):3522-28.
16. Berrios M, Skelton, RL. Comparison of purification methods for biodiesel. Chemical Engineering Journal, 2008; 144(3):459-465.