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Degumming of Pongamia Pinnata by Acid and Water Degumming Methods

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Abstract: Bio-diesel produced from the non-edible oil is one of the best methods for overcoming the problems of pollution and energy crisis. Bio-diesel obtained from Pongamia Pinnata provides viable option as an alternative fuel, especially in subtropical countries like India. Pongamia Pinnata can be used as alternative fuel for the standard diesel engines if its viscosity has been lowered before entering into fuel injection system. Apart from that it should have a low content of phosphorus and alkali earth metals such as Ca and Mg. Storage of oil for long time can lead to formation of gums if phosphorus content is more than 50 ppm. These gums can lead to choking of fuel lines and injector nozzles if oil is used without processing. This paper essentially deals with removing phosphorous content from the Pongamia oil by water and acid degumming. Phosphoric acid and citric acid is used for acid degumming process. Citric acid reduced phosphorus content from 810 PPM to 22 PPM (97.28 % reduction) and Phosphoric acid reduced phosphorus content from 810 PPM to 31 PPM (96.17% reduction). Top degumming method was also performed on Pongamia which provided best results, reducing Phosphorus content from 810 PPM to 14 PPM (98.27 % reduction). Minimum yield loss was obtained as well producing 98.1% of yield oil. NMR results confirmed that basic structure remained unaffected after the process. Hence the property of biodiesel required for engine application was retained.
Keywords: Bio-Diesel,PongamiaPinnata,Degumming,NMR,Phosphotides, Gums Etc.

Introduction:

With ever increasing shortage of liquid fuels and demands of stringent emission norms, it is absolutely necessary to find out some alternative ways for running the engine. Continuous efforts are made to develop modern age engines that match the emission norms as well. These demands also forced to give emphasis on development of alternative fuels. For achieving the mission of green planet, one such fuel which fits into such criteria is Bio-Diesel. Bio-diesel is becoming a good alternative for gasoline and diesels. Currently research is mainly focused on, to develop Liquid fuel i.e. bio-diesel[1] Biodiesel is a renewable source of energy derived from animal or vegetable based oil. It consists of long chain alkyl esters. It s made by reacting oil (either animal oil or vegetable oil) with alcohols.[3]

The fuel which is produced from the non- food generating source is called as second generation bio-fuel. These fuels essentially include non-edible bio-diesel obtained from Pongamia Pinnata, Jatropha Curacus, waste cooking oils, by products of vegetable oils etc. Out of all these plants seed , Pongamia pinnata and Jatropha curacus are found to be very rich source for biodiesel. Pongamia has been promising plant because of

its adaptabity in tropical and subtropical conditions. It shows rapid growth even in non-agricultural areas. Pongamia shows rapid growth, gets propagated easily and also shows lesser gestation period. Because of these reasons, Pongamia has emerged to be a good source of feedstock for biodiesel .Pongamia plant seeds yields about 40 % of non edible oil of India. Its oil is reported to produce the highest quality and is declared as a standard biodiesel oil as per ASTM D6751[1]

There are many fields in which biodiesel have found great acceptance. One such field is automotive industry. It is a well known fact that fossil fuel reserves are limited and increasing use of petrol and diesel fuel is a big concern. Due to depletion of the reserves, renewable and sustainable alternative fuels are looked upon and biodiesel seems to be a promising energy source. Research is being carried on biodiesel to a large extent.

However, there are some setbacks with the use of biodiesel, restraining its use on a large scale. The use of biodiesel might lead to environmental hazards as it produces pollutants. Also, the production cost of biodiesel is sometimes higher making it more expensive than petroleum based fuels.

Apart from the issues mentioned above, there is a major hurdle against the use of biodiesel in automotives: formation of gums. Gums can be formed if the fuel is kept stored for a long time. The heavier particles (gums) get deposited at the bottom. If such fuel is used in a vehicle, the gums may produce blockage in fuel lines. Gums present in piston assembly, bearings, carburetor may prevent the engine from rotating. Depending on the quantity of gums, the engine may be required to disassemble and cleaned properly. According to standards, engine used on biodiesel it must be cleaned after 150 hours.[3] If the gums are produced in large amount, then it may lead to permanent failure of the particular component.

Gums are made up of hydra table (HLP), non-hydra table phospholipids (NHLP) and other metal impurities. It comprises of phospholipids, carbohydrates, metals, proteins, water and free fatty acids. Phosphathidylcholine (PC), phosphatidyl- ethanolamine and phosphatidylinositol are classified as HLP while phosphatidic acid is NHLP[2].

HLP can be removed by water degumming process.[2] However, NHLP cannot be removed using water degumming process. In such a case, other degumming methods are adopted.

In acid degumming, various acids like phosphoric acid, citric acid can be used which transform NHLP to HLP. HLP can then be simply removed by means of water degumming methods.

Other methods such as enzymatic degumming[7], aero gel[6] methods proved to be effective in reducing phosphorous content from bio-diesel but these methods are expensive to carry out in actual conditions and also these causes more yield loss of oils. Many other methods that are widely used in industry for biodiesel production are Unilever adopted Uni degumming process[8]which combines top degumming with Super degumming, Alfa Laval developed Special degumming[9] on crude oil. Krupp uses another method called as UF degumming[10] which uses lower temp than Top and also low agitation. De Smet uses Impac degumming[11] method using additional wetting agent. This paper focuses on using cost effective method for reducing phosphorous content from Pongamia Pinnata.

Chemical property of Pongamia was studied initially by NMR and GC-MS test. Effect of various parameters on gum formations was studied by keeping the oil samples at different conditions. Preliminary degumming methods like water degumming was performed which showed slight reduction in phosphorous content. Methods like acid degumming and Top degumming gave better results as compared to water degumming method.

2. **Materials and Instrumentations:**

2.1 Materials:

Bio-diesel oil of Pongamia was taken for experimentation purpose from CO2 lab of VIT, Vellore campus Tamilnadu. Pongamia pinnata plants are cultivated in VIT Vellore campus in large numbers. The seeds of these plants are processed in order to get bio-diesel from it. H3PO4 and citric acid required for reaction purpose were obtained from Chemistry lab VIT, Vellore campus.

2.2 Instrumentations and Measurments:

a) Oil bath heating System: Various heatingprocesses required spurring the chemical reactions. The heating is provided by means of oil bath heating system. Oil bath heating system ensures simultaneous heating of number of samples uniformly

b) Magnetic stirrer: For proper chemical reactionsto take place, it was essential to have proper mixing of various acids into oil. For that purpose magnetic stirrer was used. In magnetic stirrer a magnetic piece is suspended in oil which is kept in the changing magnetic field. Because of this, suspended piece starts rotating at centre and produces vortex which provides better mixing of oil and solvent.

c) Centrifuging: After gums were produced in thesample, they formed a precipitate settling at lower part. These gums were effectively removed by means of centrifuging process, in which heavy particles settled down at bottom by centrifuging action. Centrifuging machine used for experimentation was electric motor driven with variable rpm and temperature controlled.

d) NMR(Nuclear Magnetic Resonance) - In orderto determine chemical composition of bio-diesel and to find out % of particular component present in the oil, NMR method was used. Principal behind NMR is that atom absorbs electromagnetic radiations and then emits it in magnetic field. Specific frequency at which these radiations are emitted depends on strength of magnetic field and magnetic properties of atoms[12]. NMR instrument used in this experiment have frequency range between 60-1000 Mhz.

In this experiments various NMR tests were conducted like ^{1}H NMR, ^{13}C NMR, ^{13}C NMR and ^{31}P NMR. Requirement of test is a solution containing test sample. CDCl3 was used as a solvent.

e) **Gas chromatography–mass spectrometry** -GC-MS method was used to find out exact quantityof component present in the oil sample. It combines features of mass spectroscopy and gas-liquid chromatography.

3. **Methodology:**

3.1 Gum Formation Study:

It was essential to understand various factors like formation of gums in Pongamia, the different parameters which inhibits formations of gums, the rate of formations of gums etc. In order to familiarize with the gum formation mechanism in Pongamia and governing parameters of it, initially 5 samples of oil were prepared. These samples and kept under observation in various conditions as shown in the table below.

Table No 1

Sample No	Conditions	Observation after 10 days
1	Light only	Gums produced
2	Light + Moisture	Largest Gums produced
3	Moisture only	Gums produced
4	Sample heated at 100 degree for 1 hour	Least gums formed

As shown in table no.1 after keeping the samples for 10 days, sample exposed to light and moisture produced maximum gum while the sample which was heated initially produced least amount of gums.

3.2 Water Degumming:

Hydratable gums are formed when oil absorbs moisture and causes some of the phosphatides to be hydrated. This forms a product which is insoluble in oil. Accordingly, hydrating the phosphatides in oil by adding water into it and removing hydrated phosphotides or gum is called as water degumming.[13]

As hydrated gums are removed from oil there will be little or no gum deposits on storage of oil for long time. Success of water degumming method mainly depends on hydrophilicity of phosphatides present

in the oil (1). Out of all phosphatides present in the oil mainly Phosphatidylinositol (PI), ethanolamine (PE) are hydra table easily while, PA (Phosphatidic acid) poorly hydra table and PC is non hydra table. After initial reports obtained from GC-MS test it was confirmed that Pongamia contains considerable amount of hydratable phosphotides.

Initially a sample of oil was taken and heated to 80 degree for one hour in oil test bath. Then 5 % of water was added to the heated sample and kept in magnetic stirrer for 10 min. The mixture was heated again at 80 degree for 15 minutes and then allowed to cool to room temp.

The sample was then centrifuged at 4000 rpm for 45 minutes. The final sample obtained from this process was sent for GC-MS and NMR test.

Figure.1: Water degumming reaction

3.3 Acid Degumming

Acid degumming which uses degumming acid with water can be considered as alternative to the water degumming. Acid degumming involves release of PA from its salts with an acid which is more active than PA. The degumming acid is either :

- Phosphoric acid, which forms a precipitate with Ca and Mg, or
- Citric acid, which forms a complex of Ca and Mg.

A) Acid degumming by Citric acid:

In the acid degumming, initially sample was heated at 80 degree for one hour in oil bath and allowed to cool to room temp. 2% of aqueous solution of citric acid was added into sample. The aq. solution was prepared by adding 30% by weight of citric acid powder into water.

The mixture was stirred by using magnetic stirrer for 10 min and then heated for 15min at 80 degree and allowed to cool to room temp. The sample was then sent for centrifuging at 4000 rpm for 45 min in order to separate out formed gums from

Sample.

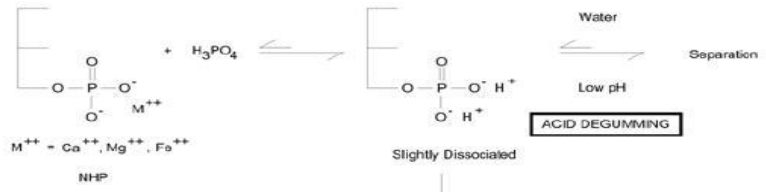

Figure.2:Acid degumming reaction

B) Acid degumming by H_3PO_4:

In acid degumming by H3PO4, initially sample was heated at 80 degree for one hour in oil bath and allowed to cool to room temp. H3PO4 (14 wt- %) was taken and 0.5 % of solution was added into oil sample. The mixture was then stirred by using magnetic stirrer for 10 min. and then heated for 15min at 80 degree and allowed to cool to room temp. This sample is then sent for centrifuging at 4000 rpm for 45 min in order to separate out formed gums from sample.

Both the samples treated with acid degumming were followed by water degumming for the removal of

hydratable gums.

3.4 Top Degumming

In conventional acid degumming method, acid like citric acid or phosphoric acid is used for decomposing the NHP followed by water degumming. But diluting this solution with water makes it weak and pH becomes lower. This makes the process reversible as shown in fig., thus converting NHPL back to HPL.[14]

In order to avoid this reverse chemical reaction one more process is introduced i.e. acid refining in which instead of diluting solution with water it is partially neutralized with adding strong alkali like NaOH. This whole process is called Top Degumming. It improves dissociation of PA, hence hydratibility is maximized.[15] This process has advantage like reduction of pollution problems due to soap stock splitting. Efficiency of this process depend on agitation agent used and type of Bio-Diesel oil.[16]

In top degumming, initially sample of oil was subjected to water degumming procedure, then 14 wt-% of phosphorous acid was taken 0.1% by vol. This solution was mixed by means of magnetic stirrer for 15 min, converting most of the NHL into HPL. Then, obtained PA was partially neutralized by means of strong alkali like NaOH. These formed phosphatides were separated from oil by centrifuging oil sample for 45 min, which was labeled as sample E.

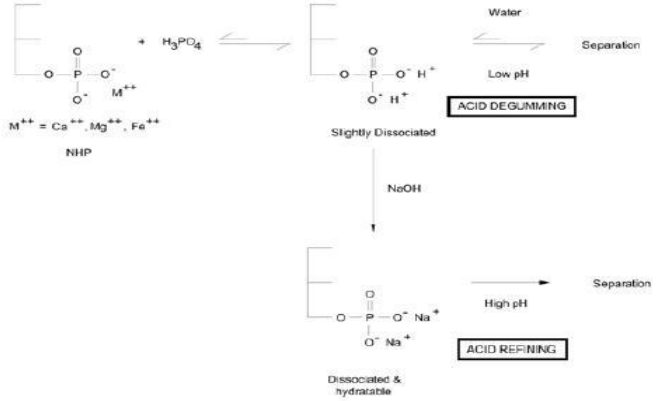

Figure.3:Top degumming reaction[2]

4. Results & Discussions:

In the degumming methods impurities like phospholipids are removed. In order to find out effectiveness of each method adopted for degumming, FFA and phosphorous contents were found out.

^{1}H NMR, ^{13}C NMR, ^{31}P NMR confirms the presence of a particular compound in a sample. However, it does not provide exact quantity of the compound present. It does indicate value of percentage reduction. GC-MS tests were conducted for all samples to determine exact quantity of a compound present. NMR results do not provide direct result. The results were processed by an advanced software MRUI-AMARES processed. The software has in-built library of probable plots for various compounds (for almost 15,000 standard compounds) . It takes the input from NMR plot, matches with the results stored in database and provide probable output[17].

4.1 Initial Sample (Sample-Zero)

All the tests mentioned above were done on a crude sample oil. It is the initial sample without any processing done. It gives value of FFA and phosphotides as shown in the table. First, the presence of various fatty acids was confirmed by means of ^{1}H NMR ^{13}C NMR and DEPT NMR. Then, exact amount of acids present in the oil werefound out by means of GC-MS tests as shown in fig. No 4.

Table No 2

Type of Fatty Acid	Chemical Composition	% quantity
Unsaturated	Oleic Acid	71.3
	Linoleic Acid	18.3
Saturated	Palmitic Acid	3.7
	Stearic Acid	3.9

As shown in table 1, Pongamia pinnata contains oleic acid as a major compound. Being present in large quantity, this compound was used as a reference to relate oil properties. From structure of Oleic acid it is confirmed that main physicochemicaland spectroscopic properties of the Pongamia oil will be related with the C=O, C-O and C=C functionalities.

Even though Pongamia Pinnata is constituted by complex mixture of triacylglycerols, oil showed well defined NMR spectra.

In the ^{1}H NMR spectrum, signals were obtained for CH2, CH3 and allylic protons of fatty acid as multiples in the region of 0.84 to 2.82 PPM. In the range of 3.72-4.23, two multiplets were observed, which were assigned to the CH and CH2 protons of the glyceryl .In the region 5.12 -5.5 PPM a broad multiplet was observed which was assigned to vinylic (=CH) protons of acid chains.

In case of 13C NMR spectrum, no. of singles were observed. Most of which were in the region 14-35 PPM representing CH2, allylic carbon atoms and CH3 group. Signals obtained at 52.08 and 78.23 PPM were assigned to the glyceryl CH and CH_2 carbon atoms, while signal obtained at 171.5-173.25PPM were assigned to the carbonyl carbon atom(C=O).

The ^{13}C –DEPT NMR signals were obtained between 13.92-14.2 PPM. This represented Carbon atoms of terminal CH3 in the fatty acid chains. Carbonyl (C=O) carbon atoms was confirmed by absence of signal at 172.35-171.25 PPM[17].

Phosphorus content in the sample was found to be 810 ppm by means of ^{31}P NMR test. by centrifuging method which gave sample D. After carrying out the process, it was measured about 9.9338 gm as shown in table. Also from 31P NMR test result of sample D it was found that phospholipids expressed as phosphorous content, was reduced from 810 PPM to 680 PPM which was still way above the acceptable level. Other tables in the paper also show corresponding change in various properties of sample D.

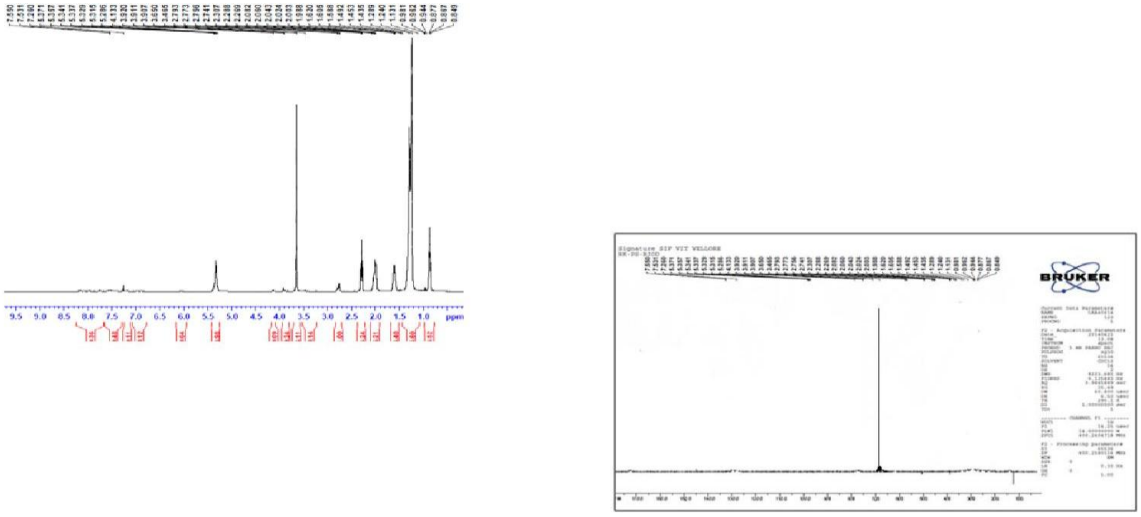

Figure.3:^{1}H NMR test result of sample-0

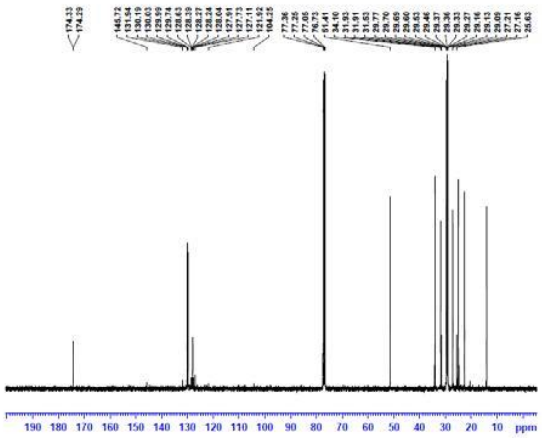

Figure.4:^{13}C NMR test result of sample-0

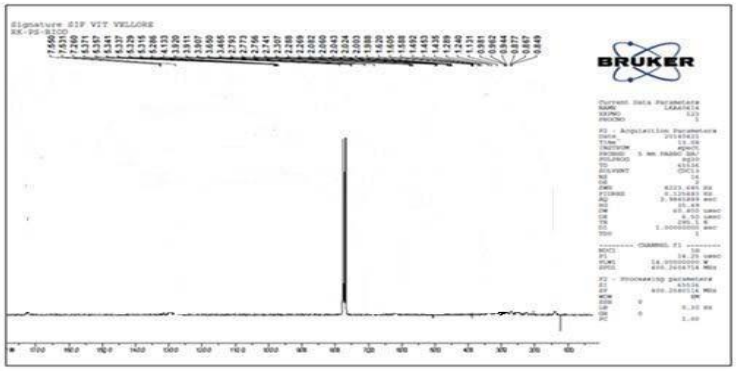

Figure.5:^{31}P NMR test result of sample-0

4.2 Normal Heating (Sample-D):

Initially, 10.0140 gm of oil sample was taken. After normal heating, some of the gums which were already formed by absorbing moisture were removed.

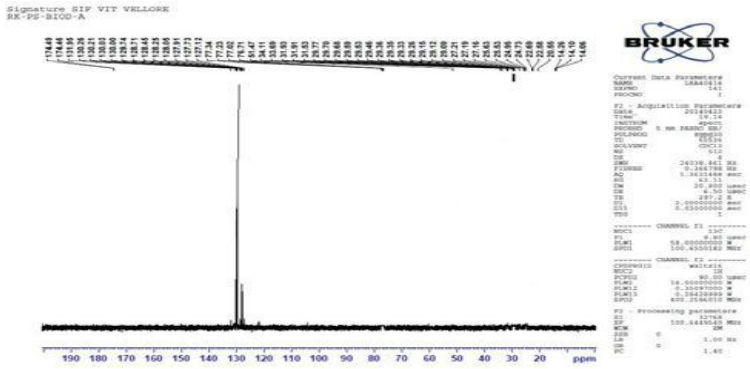

Figure.6:^{31}P NMR test result of sample-D

4.3 Water degumming (Sample C):

Initially, 10.02 gm of sample was taken and subjected to water degumming as explained earlier. In this method water reacts with HPL and forms gels. The sample is then centifuged to remove heavy particles. Crude sample of Pongamia consists of hydratable phospholipids. After water degumming, sample weighed 9.9097 gm. From results of 31P NMR test it was found that phosphotides expressed as Phosphorous content was reduced from 810 PPM to **130 PPM**.

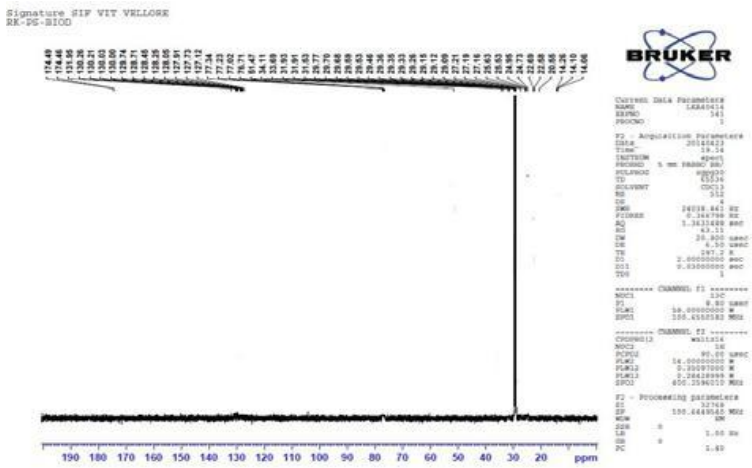

Figure.7:^{31}P NMR test result of sample-C

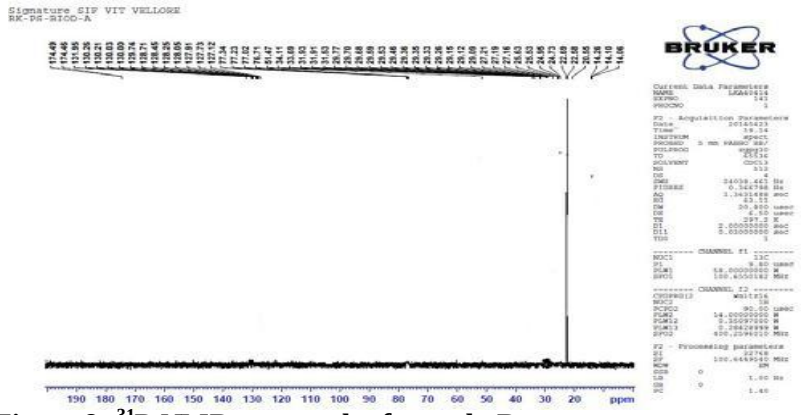

Figure.8 :^{31}P NMR test result of sample-B

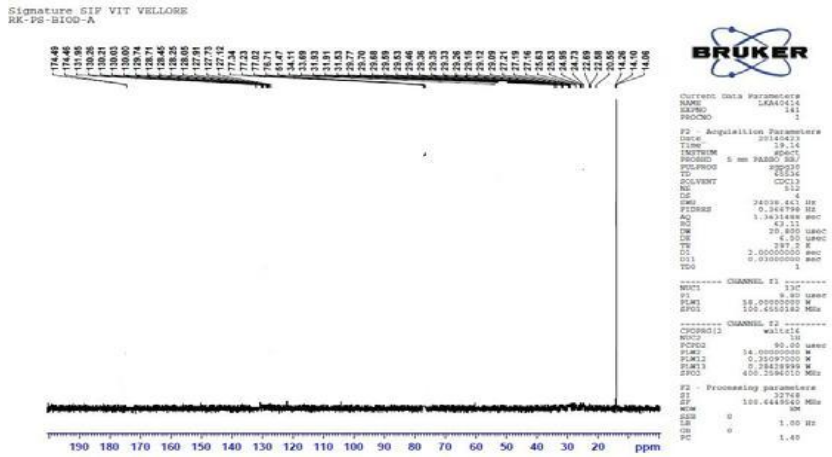

Figure.9 :^{31}P NMR test result of sample-A

4.4 Acid Degumming-Citric Acid (Sample A):

Initially, 10.015 gm of sample was taken and subjected to acid degumming with citric acid as explained earlier. In this method, NHP are converted to HPL. The resulting sample is then made to undergo water degumming process reducing HPL. Thus, more gums removal could be achieved using this method. However, loss of oil is more as well. After this degumming method, sample was weighed to be 9.7846 gm. From results of 31P NMR test it was found that phosphotides expressed as Phosphorous content was reduced from 810 PPM to 22 PPM.

4.5 Acid Degumming-Phosphoric Acid (Sample B):

Initially, 10.012 gm of sample was taken and subjected to acid Degumming with phosphoric acid as explained earlier. After this degumming method, sample was weighed to be 9.7516 gm. Also from ^{1}H NMR, ^{13}C NMR tests for sample were found to be almost similar to the NMR tests of sample 0, hence the basic structure of bio-diesel didn't changed much. However from results of 31P NMR test it was found that phosphotides expressed as Phosphorous content was reduced from 810 PPM to 31 PPM.

4.5 Top- Degumming (Sample E):

Top Degumming: Initially, 10.02 gm of sample was taken and subjected to top degumming. After this degumming method, sample was weighted which found out to be 9.6993gm. Also from ^{1}H NMR, ^{13}C NMR tests for sample were found to be almost similar to the NMR tests of sample 0, hence the basic structure of bio-diesel didn't changed much.

Test of sample E, it was confirmed that top degumming resulted in maximum reduction in phosphotides content In top degumming, reverse reaction of NHPL to HPL is restricted, which results in more removal of gums. Another advantage of this process is it results in increase of oil yield by 0.82% as shown in table. Also from 31P NMR. Phosphotides expressed as Phosphorous content was reduced from 810 PPM to 14 PPM.

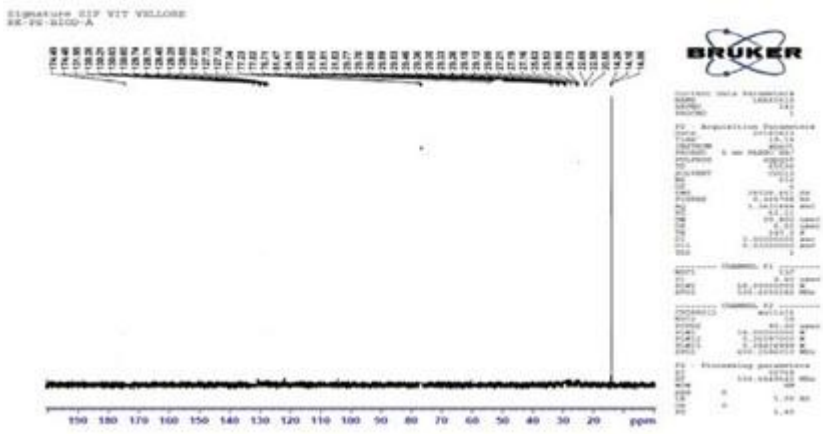

Figure.10 : ^{31}P NMR test result of sample-E

Comparing NMR spectrum of initial oil sample (0) with that of sample A-D, it was observed that number of signals and appearances were very much similar in all spectra (except 31P NMR). This confirmed that none of the oil suffered a lot in terms of fatty acids and basic composition almost remained the same as that of initial Pongamia Sample. Hence the oil can be used as bio-diesel after processing also.

%Yield= (Weight of Sample after Process)/ (Weight Of sample before process).

Table No 3 % Yield of various processes

Samples	Initial sample wt.(gm)	After Sample wt.(gm)	Yield (%)
D	10.0140	9.9338	99.20
C	10.02	9.9097	98.90
B	10.012	9.7516	97.40
A	10.015	9.7846	97.70
E	10.02	9.6993	98.10

Table No 4: Reduction in Phosphorous content

Process	Phosphorous Content (PPM)	% reduction in phosphorus From initial oil sample
D	680	16.05
C	130	83.95
B	31	96.17
A	22	97.28
E	14	98.27

5. Conclusion:

This paper was focused on studying gum formation in Pongamia Pinnata, factors governing gum formations and analyzing various degumming methods in order to reduce phosphatides from the Pongamia Pinnata. Following conclusions can be made from this paper as follows:

- In case of Pongamia Pinnata, gum formation takes place more rapidly if size of container is small.
- Pongamia Pinnata essentially consists of majority hydratable phosphotides; hence even by water degum - ming method considerable gum reduction is possible (83.95%).
- In case of acid degumming method citric acid proved to be more effective than phosphorous acid both in gum reduction and % yield point of view.
- Top degumming proved to be best method for reducing gums from Pongamia Pinnata i.e. about 98.27% reduction.
- Top degumming proved to be most cost effective method as it yields 98.10 % as good as water degumming.
- From NMR test results obtained for all the samples, it was observed that there was no significant change.

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