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Catalytic Cracking of Cottonseed's Vegetable Oil Refinery Waste-Oxidative Cleavage of Mixed Fatty Acids

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***Abstract*—Vegetable oils have not been acceptable for bio diesel production because they turn out to be more expensive than petroleum fuels in India. Relatively low cost oil refinery by products such as Soap stock/Acid oil can be used as a feedstock for the production of value added products. In the present investigation, Thermal Pyrolysis of cotton seed oil Soap stock/Acid oil which is a complex cross linked mixture of fatty acid is studied using injection of oxy-iron flame. As per literature review, the process of combustion of iron in pure oxygen and nature of products of combustion such as surface area, thickness and structure of deposited material depend on the flow rate of oxygen. The iron oxide so formed in situ may act as catalyst for pyrolysis and oxidative cleavage of mixed fatty matter are formed in cracking. These studies are intended to evaluate cracking process and characterization of products of cracking of cotton seed oil soap stock /Acid oil.**

Keywords*— *Oxy-iron flame, Soap Stock, Acid oil, Catalyst formed in situ, byproducts from refining, cracking, Oxidative cleavage, value added products

I. INTRODUCTION

The vegetable oil industry (edible as well as non edible) plays an important role in catering agricultural, dietary, food, cosmetics and chemicals, fuels and energy and many other needs of human kind. India has to import edible oils in large quantity to meet its dietary demand. Hence its use for non edible applications should be reduced as well as every by-product/waste stream generated during vegetable edible oil processing should be converted into value added products.

The cotton seed oil refinery is a major industry in the region of the districts of Akola, Parbhani, Nagpur and Yavatmal in the state of Maharashtra[6]. The soap stock generated as byproduct to extent of 10-15% of total processed oil [11]. The soap stock contains gossypol and is in dark color. The acid oil is also in dark color. The soap industry based on cotton seed oil soap stock or Acid oil generates highly alkaline dark/black colored nigre which causes environmental pollution and has no remedial measures [3]. Distillation of dark Acid oils to recover distilled fatty l pollution and has no remedial measures [3]. Distillation of dark Acid oils to recover distilled fatty acids results into carbonized solid residue in major quantity over distillate.

Thus, it is necessary to cleave the complex network of fatty acid, gossypol and other organic matter in soap stock /acid oil of cotton seed refinery before subjecting it to distillation. The oxidative cleavage of fatty acids is carried out by using chemical reagents like hydrogen peroxide [1, 2, and 9]. It yields products like aldehydes, hydroxyl acids, dicarboxylic acids etc. [2, 12]

The oxides of metals are used as catalysts for cracking of vegetable oils, soaps. Iron oxides are types of such catalysts [1, 8]. The oxidation of iron is highly exothermic process.

$2Fe(s) + 3/2\ O_{2\,(g)} = Fe_xO_y$ (Fe_2O_3, Fe_3O_4, FeO)

ΔH_f = (-800) KJ/mol to (-1000) KJ/mol

Oxy-iron flame can be obtained by blowing pure oxygen through an iron filled heated tube such as iron torch.

The temperature of the flame is about 1900K -1850K. Iron oxide is in vapor form.

The present investigation is done on oxidative cleavage of acid oil and soap stock from cotton seed oil refinery by sub merged oxy-iron flame and then recovery of value added product by vacuum distillation.

II. CONCEPT OF PRESENT STUDY

The oxygenated cleavage of the complex network of fatty and other organic matter from soap stock / acid oil of cotton seed refinery is studied by using the exotherm and iron oxide deposited in situ of inverted oxy iron flame. It ensures the fast rate of heating so that rate of pyrolysis / cracking prevails over the rate of polymerization. The exothermic reaction is used for fast heating while oxides of iron formed in situ gets mixed with the feed material and may help for cracking**.**

III. .EXPERIMENTATION

The present study is carried out in following stages of experimentation.

- Study of controlled combustion of iron in oxygen and preparation of oxy-iron torch for inverted-submerged flame thermal treatment.
- Analysis of feed materials namely Acid oil from cotton seed oil refinery and soap plant.
- Blank experimentation (without thermal treatment) for vacuum distillation of Acid oil from cotton seed oil refinery and soap plant.
- Thermal treatment of feed materials by inverted oxy-iron flame.
- Acidification and washing of thermally treated Soap stock.

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- Vacuum distillation.
- Analysis of distilled products

A. Experimental set-up

a. .Fabrication of Oxy-Iron torch

The oxy-iron torch is made up of assembly of iron tube. The iron wires/fillings are filled in 8 mm diameter and 150 mm long tube with oxygen flow pipe. Oxygen flow pipe of 12 mm diameter and 300 mm length is connected with a nozzle with 2 mm diameter bore for flow of oxygen stream at one end suitable coupling to connect with oxygen regulator and cylinder.

The torch and oxygen pipe with nozzle are joined with each other by welded coupling.

Assembly of iron wire filled tube and oxygen flow pipe with nozzle make oxy iron torch.

The torch is connected to oxygen regulating valve and cylinder by high pressure steel embedded rubber pipe.

Figure 1: Torch tube filled with iron fillings

Figure 2: Detachable torch tube fitted to oxygen flow pipe

Figure 3: Oxy-iron torch assembly

b) Cracking Vessel:

It is a S.S.316 make 5 Ltr. capacity vessel. It is constructed with internal diameter 155 mm and outer diameter of 280 mm. The length of the vessel is 130 mm. It is covered with a lid having 58 mm internal dia. and 95 mm outer dia. for proper fixing with vessel. The vessel is welded to the flanges with supports at a particular height for the convenient operation and working.

(a)

(b)

(c)

Figure 4: S.S.316 make 5 Ltrs. capacity Cracking vessel and Cracking vessel assembly

c. Vacuum Distillation set up:

It is an complete assembly, consisting of 250 ml, two necked round bottom flask with socket 'B 19', 250 ml flat bottom flask with socket 'B 19', Recovery bend with socket 'B 19', Receiving adaptor (bend with vent) with socket 'B 19', Liebig condenser having effective length 200 mm with socket 'B 19'.

The two necked flat bottom flask is fitted to the recovery bend which is attached to the one end of Liebig condenser. Other end of condenser is fitted to the receiving adaptor which is fitted to collector. High pressure 8 mm dia. rubber tube is fixed to the vent and other end is fixed to the vacuum pump.

The thermocouple is fixed to the pocket of side neck of flask to measure the temperature of material in the flask. Burner's rubber tube is fixed to the LPG cylinder through gas regulator.

Figure 5: Vacuum distillation

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B. Experimental procedure and observations

The experimental process is carried out in the following ways:

a. Development of Oxy-iron Flame

Design of torch for steady oxy-iron flame is one of the important parts of this project. It is very important to obtain a continuous and safe oxy iron flame for submersion purpose. To achieve this goal, 30gms of iron /wire fillings were filled in 8 mm diameter, 150 mm long iron tube. The tube is connected to 12mm dia., 300 mm long pipe by threaded expander coupling. The pipe is connected to control valve and flow regulator by a flexible rubber tube to oxygen cylinder. The oxygen flow pipe is welded with clamping/holding pipe of 12mm diameter and 150 mm in length to direct the flame safely. The tip of torch tube is heated in coal fired laboratory furnace till it becomes red hot and oxygen is flown at control rate. The red hot iron fillings start burning with white flame as oxygen is flown. It is found that the length of the flame, rate of burning of the torch and vigorousness of combustion depends on the flow of oxygen. The torch is held at the clamping rods by hands and can be directed towards the cracking vessel. All safety precautions like use of hand gloves, goggle, apron, shoes are followed.

A steady safe oxy-iron flame was developed using the above set-up.

Figure 6: Steady, safe oxy-iron flame

b. Analysis of Feed material

The following byproducts of cottonseed oil refining process were procured from M/s Narendra Solvex Ltd., village Dhaba, Yavatmal Road. Amravati Dist and were analysed.

The observed values are given in following tables:

TABLE I. Chemical Analysis of Soap Stock of Cotton Seed Oil

Total Fatty Matter (T.F.M)	**Moisture (%)**	**pH**
35	7.35	Highly alkaline

TABLE II. Composition of fatty acids

Myristic (14:0)	0.5 - 2.5
Palmitic (16:0)	17-29
Stearic (18:0)	1-4
Oleic (18:1)	13-44
Linoleic (18:2)	33-58
Linolenic (18:3)	0.1-2.1

TABLE III. ANALYSIS OF ACID OIL

Iodine value (I.V.)	Saponificaton `value (SAP)	Acid value (A.V.)	Moisture content (%)	pH
125	175mg KOH/gm	168.3 mg KOH/gm	10.04	Acidic

C) Blank Experimentation (Thermal pyrolysis) of byproducts of cottonseed oil refining process

In the batch Vacuum distillation apparatus, 100 ml of feed materials were heated upto 350^0 C under about 100 mm Hg till the mass becomes carbonized. It is found that the process leads to predominately to a polymerization reaction. During the stage, appreciable quantity of water gets condensed as distillate and the material in the heating flask gets carbonized. No pyrolysis takes place during the batch heating.

It can be concluded that the rate of heating should be high enough to cause pyrolysis rather than polymerization.

D) Thermal treatment of soap stock with submerged oxy-iron flame

Thermal treatment of feed material was done by submerging oxy-iron flame in it. The measured quantity of feed material was taken in S.S. 316 vessel. The oxy-iron torch was filled with iron wire/filings (measured 30gms) and its tip was heated in a furnace until it becomes red hot. At the same time, oxygen key was opened to get steady oxy-iron flame.

The oxy-iron flame is directed into the vessel containing 500 gms of feed material. The time required to complete the thermal treatment was about 1 min. 40 secs. It is observed that it is necessary to repeat the thermal treatment process three times to obtain the better results.

7a)

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7b)

Figure 7(a,b): Thermal treatment of feed material with submerged oxy-iron flame

E) Acidification of oxy-iron flame treated fatty matter

Acidification of fatty matter is necessary to convert the oxy-iron flame treated matter into fatty acids. It is done by adding drop by drop sulfuric acid (H_2SO_4) to obtain pH 2-4 of fatty matter. The sample is mixed well with the help of stirrer and settled down. The water is decanted. The fatty matter is washed to remove excess free acid and is ready for vacuum distillation.

F) Vacuum distillation

Vacuum distillation is carried out with the help of ½ HP vacuum pump. Acidified washed sample was taken in a 250 ml flat round bottom flask vacuum distillation assembly.

Heating was given by a LPG burner. The time required to complete the distillation was 1hr. 30 mints. In the process, after initial dehydration, vapors starts from 120^0C and continued up to 250-270^0 C. The distillate stopped at 270^0 C. It was also observed that the distillates get condensed in a solid form instead of liquid and was collected in round bottom flask.

The yield of 30 to 40% of oxy-iron flame thermally treated acidified fatty matter was obtained in the process.

G) Thermal Treatment of Acid Oil and recovery of product of distillation

The above procedure was repeated with acid oil as feed material. The process steps were thermal treatment with oxy iron flame and vacuum distillation of products.

TABLE IV. ANALYSIS OF DISTILLATE PRODUCTS OF THERMALLY TREATED SOAP

Sr no.	Tests	Method/Technique	Results	Unit
1.	Slip point	AOCS Cc 3 - 25	45	°C
2.	Acid Value	AOCS Cd 3d - 63	198	mg KOH/gm
3.	Hydroxyl value	AOCS Ca 13 - 60	18.36	mg KOH/gm
4.	Iodine value	AOCS Tg 1a -64	83.32	mg Iodine/100g
5.	Fatty Acid Composition	By GC		
	C 14:0 (Myristic)		1.6	%
	C 16:0 (Palmitic)		35.0	%
	C 16:1(Palmitoleic)		1.1	%
	C 18:0 (Stearic)		3.1	%
	C 18:1 (Oleic)		25.1	%
	C 18:2 (Linoleic)		31.9	%
	C 18:3 (Linolenic)		0.4	%
	C 20:0 (Arachidic)		0.5	%
	C 22:0 (Behenic)		0.3	%
	unknown		1.0	%

TABLE VI. COMPARISON OF SATURATION REACTIONS

Sr. no	Fatty acids	Cottonseed oil	Partially hydrogenated	*Partially Oxygenated
1.	Palmitic (16:0)	24.4	22.5	35.0
2.	Oleic (18:1)	17.2	50.0	25.1
3.	Linoleic (18:2)	55.0	20.3	31.9

IV. RESULT AND DISCUSSIONS

Batch vacuum distillation or thermal pyrolysis under vacuum didn't yield any value added distillate but water mainly. Formation of polymerized/carbonized mass indicates a complex condensation reaction. The same was observed for all types of feed material. However after thermal treatment by oxy iron flame, both the feed materials (acid oil and soap stock of cotton seed oil refinery) yield about 35 to 40% of yellowish-white soft fatty acids which can be used for cosmetics, lubricants and plasticizers.

The stable/steady oxy-iron flame is developed and is safely used for inverted submersion in the feed material for fast high temperature thermal treatment of feed material.

Three cycles of thermal treatment for about 100 seconds cycle time of the designed iron torch gave about 40% distilled fatty acids from thermally treated (soap stock) feed materials and 35 to 40% from acid oil as feed stock.

The analysis of product from soap stock feed material show about 45% of C16 (Palmtic) fatty acid and 47% of C18 (Oleic, Linoleic, Linolenic) fatty acids while the product of acid oil feed material show about 35% of C16 (Palmitic) fatty acid and 60% C18 (Oleic, Linoleic, Linolenic) fatty acids.

It shows cracking takes place predominantly in case of sodium salt of fatty acid (soap) over mixed fatty acids as feed material.

TABLE V. CHEMICAL ANALYSIS

Tests	Acid Oil of Cotton Seed (%)	Distillate Product of Soap Stock (%)	Distillate Product of Acid Oil (%)
Slip point	32	40	45
Acid Value	168.3	182.85	198
Hydroxyl value	5.5-25	27.98	18.36
Iodine value	125	71.43	83.32

As seen from table VI, C18 (Oleic, Linoleic acid, Linoleic) content are reduced due to oxidative cleavage of fatty matter of acid oil/soap stock and C16 (palmitic) content are increased.

The oxidative cleavage of soap stock is predominant over acid oil.

The unsaturation of the feed stock is reduced as iodine value shows decrease and melting point increases after processing. The saturation of unsaturated matter takes place due to oxidation during the process.

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IV. CONCLUSION

- The Soap stock of cottonseed oil refinery is different than other conventional edible oils. It is a complex cross linked mixture of fatty matter having low cost and cause greater environmental hazards in further processing like soap making.
- The batch vacuum distillation/pyrolysis does not yield any quantity of value added products.
- Oxy-iron thermal treatment is more effective in terms of time of process; ease of distillation, quality of distillate with minimum environmental hazards. The partial oxygenation and cleavage results into value added quality, distilled fatty acids.
- The ease of separation of distillates after thermal treatment and partial oxidation indicates that the complex network of fatty matter of soap stock from cotton seed oil is oxidative cleavage. The process of oligomer formation or condensation is also inhibited during distillation and C16 (Palmitic) content are increased while C18 (Olelic, Linoleic, Linolenic) contents are reduced.
- After thermal treatment by oxy iron flame, both the feed materials (acid oil and soap stock of cotton seed oil refinery) yield about 35 to 40% of yellowish-white soft fatty acids which can be used for cosmetics, lubricants and plasticizers.
- The yield is higher in case of soap stock cleavage than acid oil.

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