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Critical Review on Value Added Products from Cracking of Waste Vegetable Oil

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Abstract - For biodiesel or other chemical derivative preparation vegetable edible oils are not acceptable because they are shortage and more expensive than petroleum fuels. So rising in prize of petroleum, as well as the concerns about global climate change and energy security, biofuels are becoming increasingly relevant as a possible and potential alternative to fossil fuels.

This paper presents a brief overview of the current state of affairs of value added products including biodiesel at the global level, with a special emphasis on the going efforts of biofuel in India and also presents a detail yearly data on import of vegetable oil (Edible and non edible oil) in current.

The literature on by/waste streams from refinery industries also studied from the literature survey.

Index Terms- Scenario of edible and non-edible oil, Refinery processes yearly import data on refinery wastes.

1. Vegetable oil sector in India: (1, 4, 8)

In the context of shrinking crude oil reserves, rising demand, the resultant rise in prices of petroleum, as well as the concerns about global climate change and energy security, biofuels are becoming increasingly relevant as a possible and potential alternative to fossil fuels. Bio-diesels are the promising biofuels. Generally, bio-diesels are manufactured by esterification of triglycerides of edible or/ and non-edible vegetable oils. However, instead of oils directly, the bye- products such as acid oils (mixed fatty acids) obtained from soap stock are considered as economics favoring raw materials. Similarly, other value added products can be derived from the bye/waste streams of vegetable oil refinery. Keeping in view these facts, this paper presents a brief overview of the current state of affairs of value added products including biodiesel at the global level, with a special emphasis on the going efforts of biofuel in India. India is not self sufficient in edible oil production and depends upon large quantities of imports of palm oil and other vegetable oils to meet the domestic demand. However utilizing non-edible seed oils extracted from the tree has potential. Every year around 1.2 million tones of tree born seed oil are produced in the country. Biodiesel in India is also produced from oil extracted from the seeds of shrubs like Jatropha and Pongamia.

India is a leading player in edible oils being the world's largest importer and consumer ahead of the China and EU. The National council of Applied Economic Research has projected the demand for edible oils under three scenarios on the basis of per capita income growing annually by 4%, 5% and 6%.Under the low growth scenario, the demand was to rise to 22.8 million tonnes, under medium growth scenario to 25.9 million tones and under high growth scenario to 29.4 million tons in the future.

The Solvent Extractors' Association of India has compiled the import data of Vegetable oils (edible & non-edible) for the month of June 2014. Import of vegetable oils during June 2014 is down by 4% and reported at 883,679 tons compared to 947,591 tons in June, 2013, consisting of 860,736 tons of edible oils and 22,943 tons on non-edible oils. The overall import of vegetable oils during Nov'13 to June'14 is reported at 7,082,220 tons compared to 7,145,060 tons.

Table 1 (a)
Import of Veg. oil (Edible & Non edible oil) in 2013-2014: (15, 16) (Qty in M.T)

2013-14			
Month	**Edible**	**Non edible**	**Total**
Nov' 13	927.111	17,198	944,309
Dec'13	1,052,550	15,159	1067,709
Jan'14	871,527	34287	905,814
Feb'14	569,544	9,431	578,975
Mar' 14	832,925	2,499	835,424
Apr' 14	819,435	13,325	832,760
May' 14	1,022004	11,546	1,033550
Jun' 14	860,736	22,943	883,679
Total	6,955832	126,388	7,082,220

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Table 1 (b)
Import of Veg. oil (Edible & Non edible oil) in 2013-2014: (15, 16) (Qty in M.T)

2012-2013				
Month	**Edible**	**Non edible**	**total**	**%charge (2012-14)**
Nov' 13	676,234	24,137	700,351	(+) 35%
Dec'13	883,489	25,098	908,587	(+) 18%
Jan'14	1,132,631	24,499	1,157,130	(-) 22%
Feb'14	954,176	14,999	969,175	(-) 40%
Mar' 14	850,906	38,509	889,415	(-) 6%
Apr' 14	641,327	13,500	654,827	(+) 27%
May' 14	892,066	25,898	917,964	(+) 13%
Jun' 14	911,091	36,500	947,591	(-) 4%
Total	6,941,920	203,140	7,145,060	(-) 1%

2. Vegetable oil Extraction and processing: (2, 15)

Solvent extraction is a process to extract the oil from oil bearing materials by means of a solvent hexane, a byproduct of petroleum. The solvent extraction plant is designed to extract oil directly from the oil seeds containing less than 20% oil like soybeans after flaking.

3. Refining process: (1, 15, 8)

Refining of vegetable oils is essential to ensure removal of gums, waxes, phosphatides and free fatty acids (FFA) from the oils, to impart uniform color by removal of coloring pigments and to get rid of unpleasant smell from the oil by the removal of odiferous matter. During refining, the FFA is removed to the level of less than 0.1 percent in the refined oil either by chemical or physical refining. Where appropriate, preference should be given to physical rather than chemical refining of crude oil as the bleaching earth used in this process has a lower environmental impact. Conversely, chemical refining results in a better product quality in terms of lower FFA levels, longer shelf life, and a more reliable process.

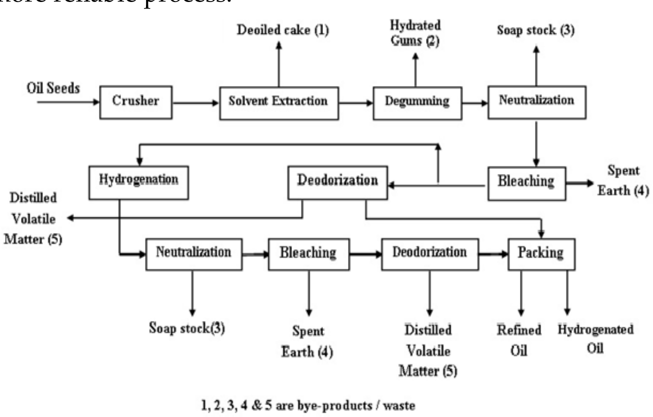

Figure 1: Steps in Vegetable Oil Refinery

Physical refining is a more simple process in which the oil is degummed and bleached, and then steam stripped to remove FFA, odor, and VOCs all in one step. A physical pretreatment can be used to achieve low phospholipids content by degumming and using bleaching earth. Previous neutralization stages are not necessary because the neutralization and deodorization are combined. A scrubber is then used to condense the greater part of the fat from the vapors as a water-free product. Most installations carry out hydrogenation to produce fats with superior retention qualities and higher melting points. Hydrogenation is usually carried out by dispersing hydrogen gas in the oil in the presence of a finely divided nickel catalyst supported on diatomaceous earth. The resultant hydrogenated fats are filtered to remove the hydrogenation catalyst, subjected to light earth bleach, and deodorized before they can be used for edible purposes. After hardening, the oil is mixed with an aqueous solution to produce an emulsion. The emulsified mixture is then pasteurized, cooled, and crystallized to obtain the final product.

Interestification involves the separation of triglycerides into fatty acids and glycerol followed by recombination. The reaction is carried out using phosphoric or citric acid with a catalyst, typically sodium methoxide. Interestification modifies the functional properties of the treated oil and may be carried out after neutralization or deodorization. During deodorization, the bleached oil is steam-distilled at low pressure to remove volatile impurities, including undesirable odors and flavors. Volatile components are removed from the feedstock using steam in a process. The vapors from the deodorizer contain air, water vapor, fatty acids, and other variables. This process produces the fully refined, edible oils and fats.

Table 2
Features of Physical Refining and Chemical Refining :(2, 6)

Physical refining	Chemical Refining
• High refinement rate; less oil loss	• Excellent adaptability and fewer requirements for high oil quality
• No waste water discharged	• The finished oil is consistent and stable
• More FFA distilled	• Less bleaching earth necessary compared with physical refining.
• Especially suited for highly acidic oils and those of low gum content.	

Table 3
The By-products/Waste streams removed from refining processes and its quantity (16)

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4. Present Usage of by-products/ Wastes: (15, 16)

A. Degumming: (1, 15, 8)

Sr. No	Refining Steps	Products removed/reduced	% Loss	Composition of products
1.	Degumming/Washing	Hydrated gums with following constitutes: 1. Hydratable non-oil materials, mostly carbohydrates and proteins partially removed 2. Hydratable non-glyceridic lipids such as phospholipids partially moved 3. Chlorophyll (partially removed),especially if phosphoric acid is employed	0.6 – 2.0%	Gums → 20 - 80 %
2.	Alkali refining	Saponified fatty matter containing following constituents: 1. Free fatty acids and other materials removed. 2. Residual phospholipids removed. 3. Proteinaceous materials reduced. 4. Coloring matter reduced.	1.6-2.0 * FFFA %	(T.F.M) → 35-85% Water content → 1060%
3.	Bleaching	Spent Earth containing following constituents: 1. Carotenoids removed. 2. Chlorophyll and its decomposition products removed. 3. Gossypol-like pigments removed. 4. Toxic agents, such as polycyclic aromatic hydrocarbons removed(if carbon is used in quantity)	0.5 - 2.0%	Spent Earth → Inorganic (ash content) = 50.42% Organic matter = 47.77% Moisture = 1.8%
4.	Deodorization	Volatiles collected in catchall containing following: 1. Free fatty acids, peroxide decomposition products, colour bodies and their decomposition products eliminated. 2. Sterols and sterol esters reduced. 3. Tocopherols reduced. 4. Pesticide residues and mycotoxins removed totally	0.1 - 0.2%	Tocopherols = 11-17% Sterols = 22%

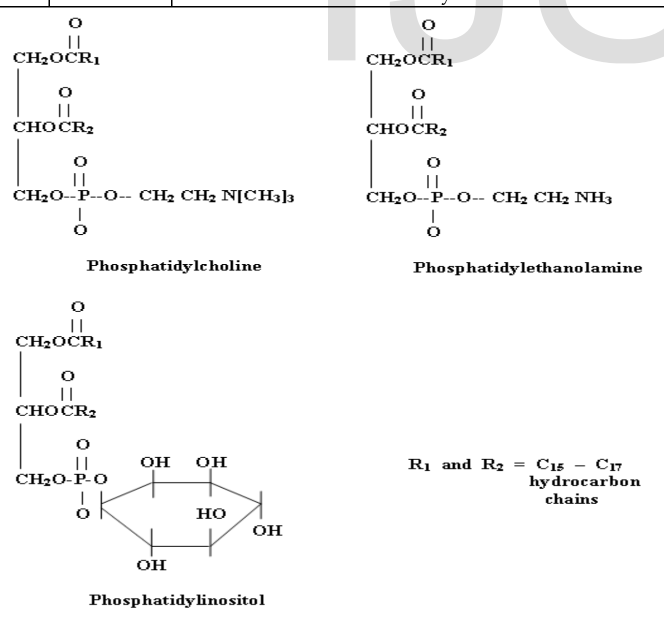

Figure 2
Chemical Formulas of 3 Major Phosphatides in Commercial Soybean Le

In this process, the phospholipids are found. The major uses of these phospholipids (gums) are as emulsifier in food products and chocolates.

In soybean oil processing, the sludge obtained. It is a mixture of several phospholipids, oil carrier and other ingredients. After drying, this mixture is marketed as commercial Soybean lecithin. It has wide application as a wetting and emulsifying agent.

B. Alkali Refining :(1, 3, 15)

In this process, soap stock is the main by-product. Most of the acidulated soap stock is used as a high energy ingredient in animal feed.

Depending upon the market demand, acidulated soap stock is separated into fatty acids by distillation as a valuable by-product of oil refining. Residue from this distillation is a good source of sterols, almost 30%.

C. Spent Bleaching Earth :(1, 3, 15)

It is a mixture of clay and oil. It has to be handled with care because it is inflammable. Processors add it to animal feed and the oil adds calories and clay reduces caking.

It is also be burned as a fuel, mixed with organic materials and composted or disposed of in a landfill after treatment with water to reduce flammability.

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D. Deodorizer distillates :(1, 15, 11)

It contains tocopherols and sterols. Tocopherols are used to manufacture Vitamin E and other antioxidants.

Sterols are used in the pharmaceutical industries for the production of many drugs including hormones and steroids.

5. Other value additions from By-products/Wastes: (1, 2, 12)

The literature survey shows biodiesel can also be prepared from soap stock obtained from the vegetable oils refinery as waste (acid oil). In India, vegetable oils are a rich part of diet. Hence, relatively high cost renders the resulting biofuels unable to compete with petroleum derived fuels. The soap stock (SS), byproduct of vegetable oil industry which contains up to 70% fatty acid is investigated to produce biofuels and also can be considered as a potential source. This could increase availability of biodiesel while decreasing its cost.

Ayhan Demirbas (6) also studied biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol tranesterification. Vegetable oil fuels had not been acceptable because they were more expensive than petroleum fuels. With recent increase in petroleum prices and uncertainties concerning petroleum availability there is renewed interest in vegetable oil fuels for diesel engines. He has found that only soap pyrolysis product of vegetable oils can be used as an alternative diesel engine fuel.

Michael J. Hass at el (4) studied the engine performance of biodiesel fuel from soybean soap stock, It has been concluded that, by means of simple chemical methods, a low quality under-utilized feedstock can be used to produce biodiesel that is compositionally comparable and functionally identical from highly refined, food grade, soybean oil but which may have a much lower cost.

V. Madhusudhan Rao (1) studied bio-diesel from vegetable oil refinery waste. The author has used the soap stock which contains 70% of fatty acid to produce bio-diesel. It was reported that oil containing high percentage free fatty acid cannot be effectively converted into bio-diesel. Also the author has studied the fuel characterization and the characterization of catalyst, percentage conversion and percentage yield and effect of parameters like time, weight percentage of catalyst. It has been found that, the process is a heterogeneous two stage catalytic and is very effective and easy to handle claimed that if the process is further explored the most of the available soap stock can be converted into useful biodiesel.

Shalini Biswas at el (2) studied the catalytic cracking of soybean oil with zirconium complex chemically bonded to alumina support without hydrogen. In absence of H2 various catalysts reportely produced over 70 components includes gases, non-condensable organic gases, unsaturated gases and liquids, aromatic and oil residues. With the use of this complex catalyst, it is reported that only liquid product with total absence of residues and non-condensable gases are produced.

Yiqin Wan at el (3) studied the effect of catalyst including the metal oxide on product selectivity by microwave-assisted pyrolysis of corn store and aspen wood. The author has concluded that some catalyst improves bio-oil yields and simplified the chemical compositions of the resultant bio-oils and improves product selectivity of the microwave-assisted pyrolysis and it is possible to control the product profiles by varying the catalyst and its dosages.

V. R. Wiggers at el (5) also studied the biofuels from continuous fast pyrolysis of soybean oil. The experiments were carried out in the range of 400 to 600 0C. The physical and chemical analysis showed that biofuels are similar to fossil fuels. Mass and energy balances were carried out in order to determine the vaporization enthalpy and the reaction enthalpy for each experiment. The thermal analysis showed that it is possible to use the product as an energy source for the process.

Ruengwit Sawang Keaw at el (7) also studied the complex catalyst, ZnO/Al_2O_3 and CaO/Al_2O_3. CaO/Al_2O_3 as the heterogeneous catalyst under the optimal conditions in the laboratory. La_2O_3/Al_2O_3 catalyst displayed a slightly higher initial activity and had potentially greater durability than that of the CaO/ Al_2O_3. It is reported that the catalyst is a promising catalyst for biodiesel production using hydrated ethanol as a feedstock by comparing the technical and economic benefits together.

6. Special case for Cottonseed oil Refinery: (1, 3)

Cotton seed oil is cooking oil which is extracted from the seeds of cotton plant of various species. An underlined seed composition is about: 8-10% of lint, 18-22% of oil, 30-35% of meal and 30-35% of hulls. In order to extract oil from cotton seeds, firstly seeds are cleaned into shaker room. Post cleaning, the cleaned cotton seed is passed through the grin sand for the removal of linters from the cotton seed. As a next step cotton seeds are passed through hullers for the removal of tough seed coats. The seeds crushed in Expellers. This helps in the partial oil recovery from the seeds. After crushing the seeds the oil is extracted and the left over pulp is called as the cake. The oil contained in this cake is recovered by solvent extraction.

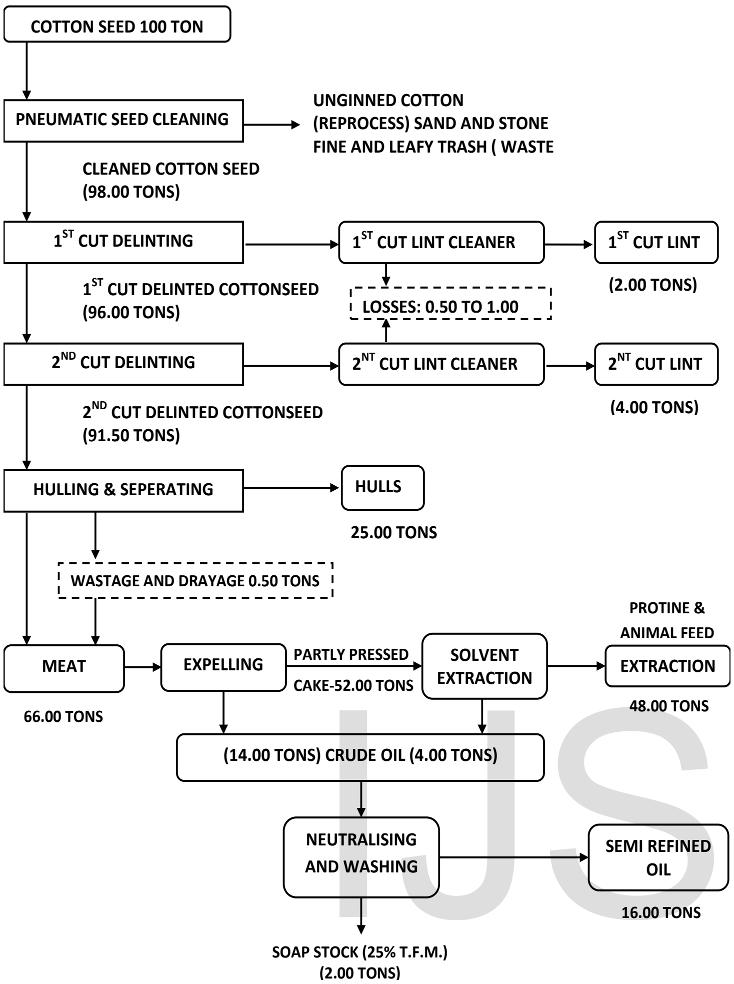

Figure 3

Material Balance of cottonseed Processing plant

7. Cottonseed Oil Processing: (1, 2, 15)

Refining: The term refining refers to any purification treatment designed to remove FFA, phospholipids, gossypol and other gross impurities in cottonseed oil. It excludes any other process such as bleaching or deodorization. The refining process has more impact on a vegetable oil's quantity and economic performance than any of the other processes during the conversion to a finished product. The refined oils will affect the operation of all succeeding processes and the quality of the finished product.

Cottonseed soap stock samples, collected during the crushing season from oilseed extraction mills throughout the United States Cotton Belt, were analyzed by chemical and chromatographic methods. Volatiles averaged 48.7±10.6%. On a dry basis, the samples averaged 33.3±7.3% fatty acids, 26.3±6.9% phospholipids, 8.4±6.4% triglycerides, and 7.5±3.0% gossypol. The analytical techniques accounted for 93.3±8.6% of the dry soap stock matter. The gossypol content is more in cottonseed soap stock.

Recognition of gossypol's role as a fertility control agent heightened interest in polyphonic compound. Caustic refining segregates gossypol into the Soap stock to levels high enough to impact its use in animal feeds. After refining, the active earths employed in bleaching are effective in gossypol removal. Deodorization, by purging the oil with live steam under vacuum removes many impurities and odor causing compounds. Analyses have indicated that, alkali refining and bleaching reduced the gossypol content of cottonseed oil to less than 1 ppm from 0.05% to 0.42 % in solvent extracted oil and 0.25 % to 0.47% for screw- pressed oil.

Cottonseed oil is unique among the presence of a relatively complex system of pigments. Most of the pigments are of the gossypol type. During seed processing, the glands are ruptured, allowing the gossypol and other similar substances to mix with the protein and oil. For the oil processor, most of the gossypol is bound to the protein. However, because gossypol and its chemically related compounds are strong pigments, it is a major objective during caustic refining

And bleaching processes to remove as much of the pigments as possible. Gossypol compounds give crude cottonseed oil; a red color of refined, bleached and deodorized cottonseed oil is primarily caused by the remaining gossypol after processing.

The different refining systems are currently used to refine vegetable oils namely chemical and physical refining. Some shortcomings are experienced with refining of cotton seed oil. The cottonseed oil contains non glycerides materials that cannot be removed by the processes employed with physical refining. Gossypol and related pigments in cottonseed oil readily combine with caustic soda and thus are removed most effectively by alkali- refining. The soap stock so obtained contents more of gossypol is in a semi solid form. All other refining processes are similar to the refining of other vegetable oils.

8. Utilization of by-products/waste: (1, 15)

First and second cut Linters, Hulls, Cake Soap stocks are major bye products or waste streams. Microcrystalline cellulose, cellulose powder, acid oil, Soap, recovery of gossypol. Biogas, cattle feed cracking of acid oil etc. are some of routes of utilization of bye-products/waste from cottonseed processing industry.

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