Oleochemicals from Coconut Oil

Coconut, the most important among plantation palms, has emerged in recent times as oil, food, beverage, fiber and timber crop, which is rightly eulogized as '*Kalpa Vriksha*'. Every part of the coconut palm is used by mankind in one way or other and testimonializes its importance as a crop of multifarious use. Even though oil is the most important commodity product obtained from coconut, it yields numerous other value added edible and inedible products.

It is estimated that in India about 10 million families are involved and economically benefitted from coconut cultivation, processing and marketing activities. Apart from coir products, the export of other coconut product is quite insignificant. Many leading coconut growing countries have attained fast progress in product diversification and by-product utilization. The Philippines is the major coconut producing country that had made giant strides in manufacturing millions of tonnes of industrially valuable oleochemicals (cocochemicals) from coconut oil and exporting to America, Europe and a few African countries and also to Russia, Japan, China, South Korea, Taiwan, Singapore and Australia. The production of coconut oil based chemicals in India, one of the leading producers of coconut, is negligible and insignificant compared to the Philippines. Coconut oil is the single commodity around which the price of raw coconut fluctuates in the country. Thus, it is most important that utilization of coconut is enhanced through diversification of oil based chemicals and products, so that demand for coconut oil is ensured throughout the year. The annual production of coconut oil in India is 450 thousand tonnes, of which 40 per cent is for edible purpose, 46 per cent for toiletry use and only the remaining 14 per cent is utilized for industrial purposes.

Chemical Nature of Coconut Oil

The coconut oil is obtained from dried copra *i.e.*, dried endosperm of fruit of *Cocos nucifera* L, which commonly yields 65 per cent oil. Like any other vegetable oil, coconut oil consists of major amount of triglycerides, a substance comprising chemically three fatty acid molecules bound to one glycerol molecule. The composition of fatty acids of coconut oil is depicted below :

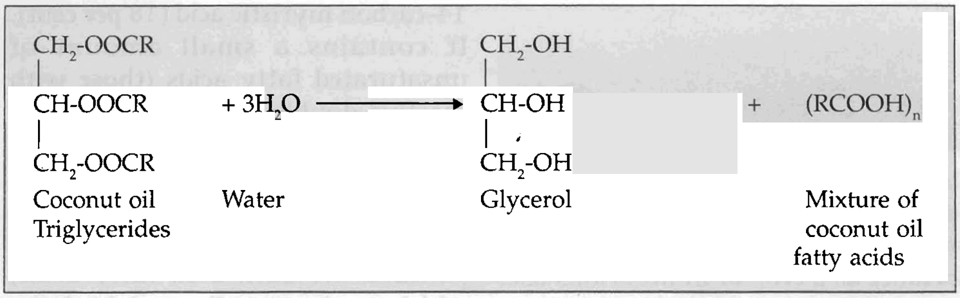
Common name	Forumula	Percentage
Caproic acid	$CH_3(CH_2)_4COOH$	0.5
Caprylic acid	$CH_3(CH_2)_6COOH$	7.2
Capric acid	$CH_3(CH_2)_8COOH$	5.7
Lauric acid	$CH_3(CH_2)_{10}COOH$	48.9
Myristic acid	$CH_3(CH_2)_{12}COOH$	18.2
Palmitic acid	$CH_3(CH_2)_{14}COOH$	8.8
Stearic acid	$CH_3(CH_2)_{16}COOH$	2.4
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	6.7
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	1.6

The nine fatty acids present in coconut oil are caproic, caprylic, capric, lauric, myristic, palmitic, stearic, oleic and linoleic. It can be seen that the major fatty acid is 12-carbon lauric acid constituting about 49 per cent followed by 14-carbon myristic acid (18 per cent). It contains a small amount of unsaturated fatty acids (those with reactive double bonds) of oleic acid (6.7 per cent) and linoleic acid (1.6 per cent), which is an essential fatty acid. The remaining seven - caproic, caprylic, capric, lauric, stearic and palmitic are saturated fatty acids, which are structurally straight chain. It is these triglycerides and composition of fatty acids of coconut oil that forms the basis for utilization of this oil for production of primary chemicals such as glycerol, fatty acids, methyl esters and fatty alcohol and further downstream oleochemicals from coconut fatty acids and fatty alcohols. Coconut oil has excellent desirable properties of high resistance to oxidative rancidity, long shelf life, biodegradability and easy saponification.

Base Chemicals from Coconut Oil

When coconut oil (triglycerides) is made to react with excess water, a process called hydrolysis, at an appropriate combination of high pressure, temperature and catalyst to attain high rate of hydrolysis, the coconut oil is split into glycerol and mixture of fatty acids. Normally, 100 g of coconut oil with 0.1 per cent moisture level will yield approximately 96 g of mixture of fatty acids and 14 g glycerol.

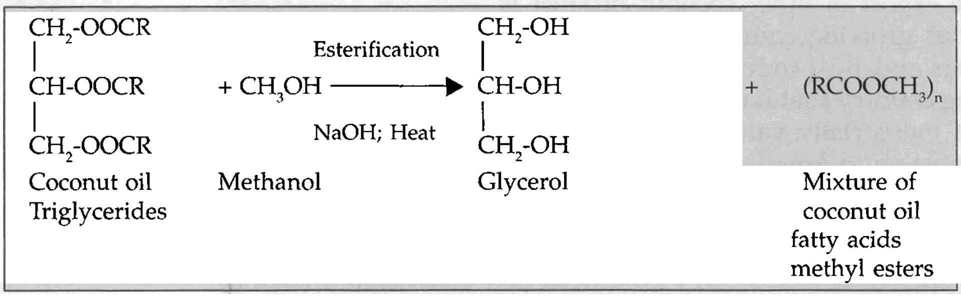
Glycerol : Glycerol is obtained as byproduct from the hydrolysis of coconut oil. It is also obtained during methanolysis of coconut oil. The glycerol is obtained in 77 per cent purity and after purification by distillation and bleaching, 99.5 per cent purity is obtained. Mainly glycerol is used in pharmaceutical and cosmetic industries as emollient and in foodstuff, resins and ester production. Glycerol is also used in nitration process of dynamites, in tobacco industry as humectant and



in antifreeze mixture. Among the vegetable oils, coconut oil has maximum content of glycerol (13.5-15 per cent).

Fatty acids : The mixture of fatty acids produced by hydrolysis of coconut oil forms one of the key intermediates and serve largely as the raw materials for synthesis of downstream oleochemicals. The versatility of coconut oil for manufacturing oleochemicals depends on the fact that the carboxyl group of these fatty acids is reactive and so it can host a series of reactions to produce other oleochemicals. From the coconut oil fatty acids, various downstream oleochemicals are produced. All these oleochemicals have various applications in industrial fields.

Methyl Esters : Methyl esters are produced by a process of trans resterification in the reaction of coconut oil and methanol. Glycerol produced as byproduct is separated by washing with water. Theoretically, when one part coconut oil react with three parts methanol, three parts coconut fatty acid methyl esters (CME) and one part glycerol are produced. Percent conversion to CME in the actual production process is about 80-90 per cent. By this method, 88 per cent ester and 12 per cent glycerol is obtained based on the weight of coconut oil. The process is-



Coconut oil fatty acid methyl esters have lower boiling point and are less corrosive than fatty acids and are generally used in the manufacture of soaps, non-soap detergents, plastics, resins, paints, varnishes, insecticides and cosmetics. Another important benefit of CME is its ability to make higher purity-finished products. Methyl esters of coconut oil are also used as an alternative fuel to diesel. In a study at Philippines, performance of vehicle engine run on methyl esters of coconut oil was same as that of diesel. In terms of fuel consumption index, CME was inferior by 15 per cent only due to lower heating value of methyl esters of coconut oil. In terms of fuel consumption, coconut oil methyl esters burnt more efficiently than diesel and CME emitted 16 per cent less carbon monoxide making it less polluting and environment friendly. The vehicle (diesel engine, 2369 cc, 4 cylinder) was found to run 8-10 km per litre.

Fatty Alcohols : These are produced from coconut oil fatty acids or methyl esters of fatty acids by copper chromite reduction (Hydrogenation) with 90 per cent conversion. The manufacturing route of fatty alcohols is illustrated in the chart 1. Fatty alcohols form the second important base materials after fatty acids for synthesis of industrially important chemicals, which have found uses in detergents, insecticides, cosmetic and pharmaceutical preparations and as plasticizer.

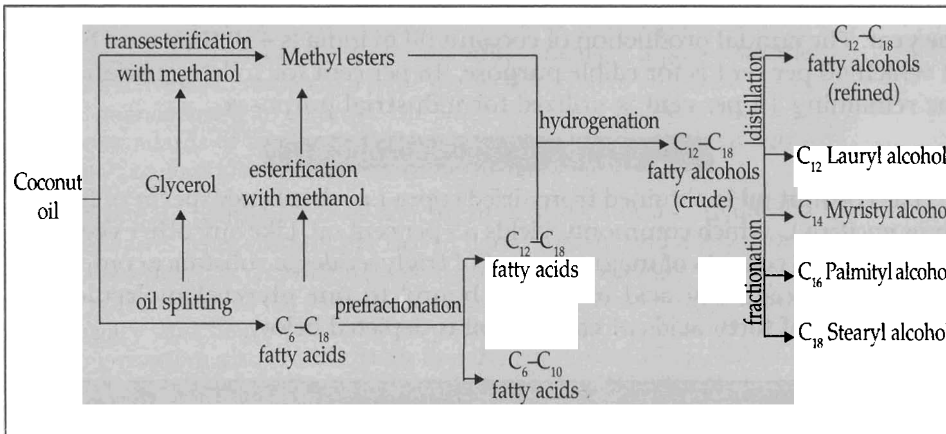
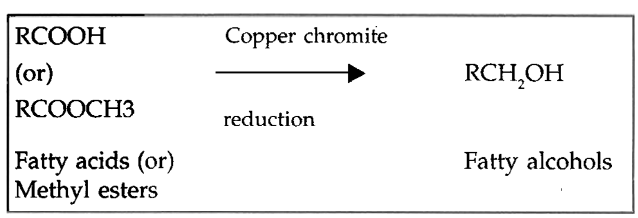


Chart 1. Manufacturing route of fatty alcohols



Fractionation of Fatty Acids : The fatty acids split from coconut oil are pre-fractionated into short chain fatty acids (caproic, caprylic and capric acids) and medium and long chain fatty acids (lauric, myristic, palmitic, stearic, oleic and linoleic acids). The lauric-stearic (C_{12}-C_{18}) acids collected from pre-fractionation as bottom product are further processed into lauric, myristic and palmitic-stearic acids. The fractionation of fatty acids from coconut oil is illustrated in the *chart 2.*

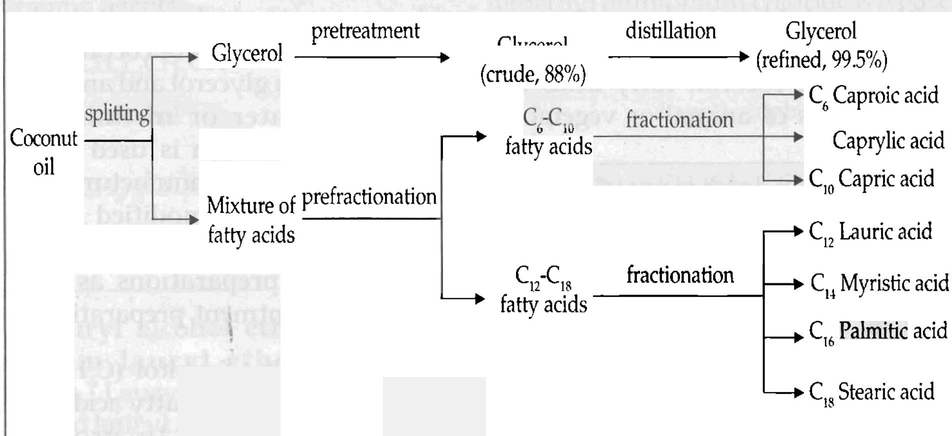


Chart 2. Fractionation of fatty acids from coconut oil

Uses of short chain fatty acids : The short chain caproic, caprylic and capric acids removed from prefractionation process can be further fractionated into individual fatty acids by distillation and used for production of various derivatives. These derivatives are ethyl caproate, amyl caproate and allyl caproate used as synthetic flavours; ethyl caprylate, amyl caprylate and butyl caprylate as perfumery intermediates; barium caprylate/caprate as stabilizer for PVC; allyl caprate as sweet banana and pineapple synthetic odours; amyl caprate as arrachcognac odour; amylose caprate as dip top coating for products; butyl caprate as apricot odour and capryl caprate for chemical pruning activities on plants. These value-added products are used as artificial fruit flavours, perfumes, perfume intermediaries, coating for food products and as pruning chemicals on plants, etc.

Uses of long chain fatty acids : The long chain fatty acids (palmitic, stearic, oleic and linoleic), which account for 22 per cent of total fatty acids, can be used for synthesizing sulphonated alpha olefins. The sulphonated alpha olefins have excellent foaming properties and used in the detergents, toilet soaps and shampoo industries.

The various downstream oleochemicals synthesized from coconut oil are outlined in flow *chart 3.*

Derivatives from Coconut Oil Fatty Acids

Coconut fatty acid esters : Fatty acids are converted into their esters by making them to react with lower alcohols in the presence of minerals and catalysts. For example, fatty acids are reacted with isopropanol to produce fatty acid isopropyl ester, which is an oil with good wetting and solvent properties and used in aerosols, cosmetics and hair care products. Coconut oil fatty acids hexyl ester is prepared by reacting fatty acids with hexanol, which has good spreading properties and low viscosity and find uses in aerosol preparations.

RCOOH	+	$(CH_3)2CHOH$	$\longrightarrow$	$RCOOCH) (CH_3)_2$	+ H_2O
Coconut oil Fatty acids		Isopropanol		Isopropyl ester	Water

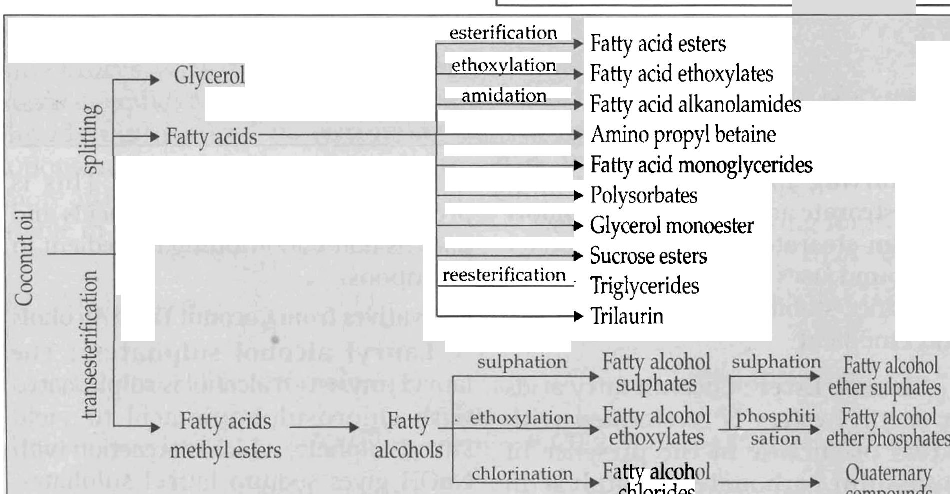


Chart 3. Synthesis of downstream oleochemicals from coconut oil

Coconut fatty acid ethoxylates : When fatty acids are reacted with ethylene oxide, fatty acid ethoxylates are produced. These ethoxylates are used as emulsifiers, lubricants and antistatic agents in food, textile, cosmetic and pharmaceutical industries.

Coconut fatty acid alkanolamides : These can be prepared directly from coconut oil or its fatty acids or methyl esters. Because of advantage of methanol being easily distilled off as byproduct, methyl esters of fatty acids are preferred. Monoethanolamides is prepared when

RCOOH	+	CH_2–CH_2 (O)	→	$RCOO(CH_2CH_2O)n$
Coconut oil fatty acids		Ethylene oxide		Fatty acid ethoxylates

one mole of coconut oil is reacted with three moles of monoethanolamine. Similarly, with diethanolamine, diethanolamides are prepared in the presence of KOH catalyst in 63 per cent purity. Diethanolamide mixture also contains esters, ester amides, and amines. Superamides of 90-95 per cent purity are obtained from the reaction of coconut fatty acids or methyl esters with monoethanolamine.

RCOOH	+	$NH_2CH_2CH_2OH$	→	$RCONHCH_2CH_2OH$	+	H_2O
Coconut oil fatty acids		Ethanolamine		Fatty acid monoethanolamide		water
RCOOH	+	$NH(CH_2CH_2OH)_2$	→	$RCON(CH_2CH_2OH)_2$	+	H_2O
Coconut oil fatty acids		Diethanolamine		Fatty acid diethanolamide		water

These are nonionic surface-active agents. These compounds have good cleaning action, high viscosity and non-rusting properties. These are extensively used as foam stabilisers, super fattening agents and as thickening agents for detergents, shampoos and cosmetics. They are also used as softening agents of fibres, antistatic compounds, dye-levelling agents and as water repellents in textile industries.

Coconut fatty acids monoglycerides : These are generally produced by the reaction of triglycerides or its fatty acid/methyl ester with glycerol to obtain a mixture of mono, di and triglycerides. Commercially monoglycerides are used as modifying agent in the manufacture of alkyl resins and detergents. They are also used in the preparation of cosmetics, pigments, floor waxes, synthetic rubbers, coatings and textiles. High purity monoglycerides have anti-staling properties, provide uniform size in baking, prevent dryness, whipping in frozen foods, and prevent oiling off in peanut products. It is also used as anti-caries agent in toothpastes.

Glyceryl Monoester : Excess glycerol is made to react with hydrogenated coconut fatty acids or methyl esters of animal or vegetable origin and the water or methanol byproduct is removed. For example, the starting materials for glyceryl monostearate are hydrogenated tallow or palm stearate. Glyceryl monoester has found uses as food and cosmetic emulsifier, stabilizer, thickener, purifier and emollient.

Sucrose Ester : Coconut fatty acids or methyl esters is reesterified with excess of sucrose in the presence of potassium carbonate as catalyst in propylene glycol solvent. Sucrose ester is a good emulsifier and has surfactant properties and low skin irritability.

Triglycerides ; The C_6-C_{12} coconut fatty acids or methyl esters are reesterified with glycerol to produce triglycerides. Three moles of fatty acids/methyl esters are reacted with one mole of glycerol and water or methanol byproduct is removed. These coconut medium chain triglycerides are used as dietary fat for patients with malabsorption syndromes.

Trilaurin : Three moles of lauric acid or methyl laureate, the predominant fatty acid of coconut oil, is esterified with glycerol and an equal amount of water or methanol is distilled out. Trilaurin is used as an intermediate in the manufacturing of shortenings and oil-modified resins and also used in the pharmaceuticals and medicinal preparations as base ingredient in ointment preparations.

Polysorbates : Sorbitol ($C_6H_{14}O_6$) is reacted with coconut fatty acids and with ethylene oxide to produce polysorbates, which is used in chocolates as emulsifying surfactant.

RCOOH	+	$C_6H_{14}O_6$	→	$RCOOC_6H_{13}O_5$	+	H_2O
Coconut oil fatty acids		Sorbitol		Fatty acid sorbitan		Water
$RCOOC_6H_{13}O_5$	+	CH_2–CH_2 (O)	→	Polysorbates		
Fatty acid sorbitan		Ethylene oxide				

Amidopropyl betaine : This is prepared from coconut fatty acids and used as hair conditioning ingredient in shampoos.

Derivatives from Coconut Fatty Alcohols

Lauryl alcohol sulphates : The lauryl (myristyl) alcohol is sulphonated with chlorosulphonic acid to yield lauryl sulphate, which on reaction with NaOH gives sodium lauryl sulphates. This is an emulsifier and foaming chemical used in bath preparations in powder form, toothpaste, mouthwash and also as wetting agent in tablets. Inclusion of lauryl alcohol sulphates makes soaps lather profusely even in hard water and seawater. Similarly, lithium lauryl sulphate, ammonium lauryl sulphate, magnesium lauryl sulphate are synthesised with their respective neutralising agent. These chemicals have good dispersing, foaming and emulsifying properties and are used as base for liquid shampoos, cosmetic bath preparations and in cleaning agents.

$CH_3(CH_2)_{10}CH_2OH$	+	$ClSO_3H$	→	$CH_3(CH_2)_{10}CH_2OSO_3H$ + Hcl
Lauryl alcohol		Chlorosulphonic acid		Lauryl sulphates
$CH_3(CH_2)_{10}CH_2OSO_3H$	+	NaOH	→	$CH_3(CH_2)_{10}CH_2OSO_3Na$
Lauryl sulphates		Sodium hydroxide		Sodium lauryl sulphates

Lauryl alcohol ethoxylates and sodium lauryl ether sulphates (SLES) : Lauryl alcohol is ethoxylated to yield lauryl alcohol ethoxylates and then sulphonated to give SLES. They are used as surfactants in many industries. This is the main ingredient in liquid shampoos, bubble bath preparations, dish-washing compositions and also included in fire-fighting concentrate as emulsifiers, solubilisers and dispersants. These chemicals are also used in making homogenous mixture of oily substances with water, dispersing solids in liquids and mixing immiscible liquids uniformly. The creams and lotions made with such surfactants are more attractive, convenient for use and stable in storage.

$CH_3(CH_2)_{10}CH_2OH$	+	CH_2–CH_2 (O)	→	$CH_3(CH_2)_{10}CH_2O(CH_2CH_2O)_n$-H
Lauryl alcohol		Ethylene oxide		Lauryl ethoxylate
Lauryl ethoxylate	+	$ClSO_3H$	NaOH →	$CH_3(CH_2)_{10}CH_2O(CH_2CH_2O)_nSO3Na$
		Chlorosulphonic acid		Sodium Lauryl Ether Sulphates (SLES)

Sodium lauryl ether phosphates (SLEP) : Lauryl alcohol ethoxylates can be phosphated to obtain SLEP. This is used as wetting agent in many preparations.

Lauryl chlorides and quaternary compounds : Lauryl alcohol is reacted with HCl to yield lauryl chlorides. This alkyl chloride on reaction with amines produces very useful quaternary compounds like lauryl diethyl benzyl ammonium chloride, which is an effective antistatic agent. Lauryl alkyl dimethyl ammonium chloride is a base for liquid shampoos and lauryl trimethyl ammonium chloride is a good wetting and antistatic agent and used as hair conditioner.

$CH_3(CH_2)_{10}CH_2OH$	+	HC1		$CH_3(CH_2)_{10}CH_2C1 + H_2O$
Lauryl alcohol		Hydrochloric acid		Lauryl chloride
Lauryl chloride	+	$^1CH_3 - N - C_6H_5$ (with $^2CH_3$ on N)	→	$CH_3(CH_2)_{10}CH_2 - N+ - C_6H_5Cl$ (with $^1CH_3$ and $^2CH_3$ on N)
		Dimethyl benzyl		Lauryl dimethyl benzyl ammonium chloride amine (Quaternary compound)

Fatty amines : Fatty amines of coconut oil and their ethoxylates find use in the textile industry as emulsifiers and softeners.

Despite India is making impressive progress in production and productivity of coconut, its contribution to the export market is insignificant. Except coir, no other coconut products are exported at economically significant level. The coconut industry survives mainly on coconut oil and it is the single commodity, which determines the price of a coconut in the country. There is a need to diversify and augment the utilization of coconut oil and the large-scale manufacturing of coconut oil based oleochemicals will be one of the promising areas, which is of course capital intensive. These cocochemicals are in high demand in international market. The scope for manufacturing industrially important oleochemicals from coconut oil on a large scale is high considering applications and utility of these derivatives in industrial and health/personal care products and export potential to developed countries as foreign exchange earner. Presently, mineral oils (known as liquid paraffins) obtained from petroleum are used as major component in cosmetics and skin care products. These synthetic oils penetrate the skin and enter human body, which is harmful to health. Efforts must be made to replace these hazardous petroleum-based products with natural oleochemials from coconut oil, which is environment-friendly and biodegradable.

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Area under and production of coconut in Tamil Nadu 2002-2003

Districts	Area	Percentage share	Production	Percentage share	Productivity
	(In ha)	%	(In lakh nuts)	%	(Nuts per ha.)
Kancheepuram	4564	1.32	144	0.50	3155
Thiruvalluar	1091	0.32	82	0.29	7516
Cuddalore	2670	0.77	357	1.25	13371
Villupuram	2118	0.61	143	0.50	6752
Vellore	18690	5.40	1713	5.99	9165
Thiruvannmalai	1023	0.30	73	0.26	7136
Salem	11720	3.39	808	2.82	6894
Namakkal	2174	0.63	210	0.73	9660
Dharmapuri	20229	5.85	1559	5.45	7707
Coimbatore	99250	28.69	6300	22.02	6348
Erode	17377	5.02	1617	5.65	9305
Thiruchirappally	5991	1.73	842	2.94	14054
Karur	4331	1.25	514	1.80	11868
Perumbalur	882	0.25	55	0.19	6236
Thanjavur	23934	6.92	2241	7.83	9363
Thiruvarur	4742	1.37	724	2.53	15268
Nagapattinam	3660	1.06	259	0.91	7077
Pudukottai	5105	1.48	256	0.89	5015
Madurai	10545	3.05	981	3.43	9303
Theni	14284	4.13	1411	4.93	9878
Dindigul	24277	7.02	2115	7.39	8712
Ramanathapuram	9120	2.64	481	1.68	5274
Sivaganga	5861	1.69	361	1.26	6159
Virudhunagar	8511	2.46	649	2.27	7625
Tirunelveli	15423	4.46	1063	3.72	6892
Thuthukudi	5586	1.61	267	0.93	4780
Nilgiris	61	0.02	0	0.00	0
Kanniyakumari	22667	6.55	3382	11.82	14920
STATE	**345886**	***100***	**28607**	***100***	***8271***

Source: Department of Economics and Statistics, Chennai