compounds is still being studied, but preliminary tests indicate the presence of a para-disubstituted aromatic system with possible presence of $-NH_2$ groups.

One of the major uses of oils is for frying. According to Lantz and Carlin (9), frying oils often are discarded when their Lovibond red color increases from 1.5-3.5 to 20-30 units. One of the problems with palm oil is that it darkens rather quickly during frying, although this does not indicate rapid oxidation and should not be used as a guide to the oil quality (10). The study of the cause of this rapid heat darkening and its prevention is important because of this.

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⁂The "Hard" and "Soft" Surfactant Profile of Israel Municipal Wastewaters

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ABSTRACT

A study of mapping and field monitoring of Israel's municipal sewage wastewaters in respect to the content, distribution and the initial nonbiodegradable-biodegradable ratio of surfactants in them has been undertaken over the central and northern parts of the country under in vivo conditions.

Typical concentrations of nonionics (mainly "hard" alkylphenol-based ethoxylates) and anionics (mainly the "soft" LABS) in influents were found to be within the range of 1.1-2.2 and 9.6-10.6 mg/liter respectively. In (treated) effluents, the corresponding concentrations are 0.3-0.45 and 0.3-4.3 mg/liter.

The above is in accordance with current world trends following the switch to biodegradable surfactants. However, the concentrations of nonionic surfactants in the municipal wastewaters are surprisingly low in view of the preferred consumption of "hard" nonionic surfactants in the local market.

It is concluded that 20-40% of all nonionic surfactants discharged into municipal sewage, additional amounts of their metabolites and some of the anionic surfactants, too, find their way into receiving waters, because they resist substantial removal via only primary and secondary treatment.

INTRODUCTION

The annual world production of all kinds of surfactants mainly for household and industrial cleaning formulations already has passed the 17 million ton mark (1,2). The extent, mechanism and rate of biodegradation of the various synthetic anionic and nonionic surface active agents (3,4) under aerobic and anaerobic conditions are critical to the pollution of water resources, with the plethora of technological and environmental consequences involved (5-7).

The increase in environmental concerns is worldwide, and the urgent need to use more reclaimed wastewaters of various sources will undoubtedly affect the future development, use and economics of the detergent industry. All kinds of surfactants (anionic, nonionic and cationic), ultimately find their way into either man-made sewage systems or natural surface and ground water bodies. Consequently, surfactants are a significant factor in the municipal sewage profile (8) which, in turn, determines both the possibility of the sewage water's reuse after appropriate purification processes and the efficiency of the latter (5). Currently, the main uses of reclaimed municipal wastewater are agricultural irrigation (restricted and unrestricted), industrial recycling (mainly for cooling and washing purposes) and ground water recharge (8-10).

In Israel, which is a model of efficient water utilization (11), natural water resources have reached almost the limit of practical exploitation. Within two years, about two-thirds the total volume of sewage collected by sewers will be used for agricultural purposes (12).

Alongside the biodegradable anionic LABS, "hard" (nonbiodegradable) nonionic surfactants of the ethoxylated alkylphenol type currently are the most commonly used nonionics in the country (13). The situation concerning household detergent formulations has no parallel in other Western industrial countries (14). Furthermore, a substantial portion of the country's municipal wastewaters is dumped directly into the Mediterranean Sea without any treatment, while the remaining portion reaches other surface water bodies after only a very brief preliminary treatment. The above facts make the determination of the surfactant content of our wastewaters imperative.

Mapping and monitoring of Israel's municipal sewage influents (15) as outlined in the Abstract would enable appropriate action on a national scale in terms of surfactant production and formulation, regulation, water resources management, future planning of the use of reclaimed treated wastewater and the protection of the environment.

RESULTS AND DISCUSSION

The concentrations of anionic (mainly LABS) and nonionic surfactants found in some representative municipal influents in the central and northern parts of the country are given in Table I. The determinations are based on the classical MBAS (16) method and the modified SDA-CTAS (17) method for the anionic and nonionic surfactants, respectively.

Since the given data represent about 60% of the collected municipal sewage, including different categories of

TABLE I

Typical Concentrations[a] of Anionic and Nonionic Surfactants in Representative Municipal Wastewater Influents[b] in Israel (Summer 1983)

Location of sewage	Anionic surfactants	Nonionic surfactants	Total	Anionic/nonionic ratio (%)
Tel Aviv (north)	10.5	2.1	12.6	83.3:16.7
Dan Region	10.3	2.2	12.5	82.4:17.6
Haifa	9.6	1.6	11.2	85.7:14.3
Hadera	10.2	1.1	11.3	90.3: 9.7
Tiberias (lower)	10.6	1.3	11.9	89.1:10.9
Average[c]	10.3	2.0	12.3	83.7:16.3

[a]Figures are mg/liter.

[b]Total volume of wastewaters represented here—is about 300,000 cubic meters per 24 hr.

[c]Weighted average in accordance with the daily volume of wastewater influents in each location.

TABLE II

Initial Nonbiodegradable-Biodegradable Ratio of Nonionic Surfactants in Israel Municipal Sewage Influents[b] (Summer 1983)

Location of sewage	Total nonionic concentration[a]		Nonbiodegradable/Biodegradable ratio %
	Initial	After a week	
Tel Aviv (north)	2.15	1.30	60.0:40.0
Dan Region	2.10	1.30	61.9:38.1
Haifa	2.45	1.80	73.5:26.5
Hadera	1.05	0.60	57.1:42.9
Tiberias (lower)	1.30	1.20	92.3: 7.7[d]
Average[c]	2.17	1.38	63.6:36.4

[a,b,c]Same as in Table I.

[d]The reason for this exceptional result is not yet clear.

urban sections, the findings are believed to be representative.

As one can see, typical concentrations of anionic MBAS (almost all of which is LABS, the dominant anionic detergent used in Israel) and nonionic CTAS in the municipal influents are within the range of 9.6-10.6 mg/liter and 1.1-2.2 mg/liter, respectively, and the total detergent con tent 9.5-13 mg/liter. This means that the share of nonionic surfactants in the detergent market in Israel is about 15% compared with about twice as much in the American market.

However, as will be shown in Table II, the portion of the nonionic surfactants in Israel consists mainly of nonbiodegradable types (i.e. branched-chain alkylphenol).

The initial ratio between nonbiodegradable and biodegradable nonionic surfactants was established by determining the concentration of the nonionic detergents immediately after sampling and a week later in the same nonpreserved samples, which were stirred at room temperature during that period (semi in vivo conditions) (8,13,15).

Based on these findings, the initial ratio between the nonbiodegradable and biodegradable nonionic surfactants was determined to be about 2:1 (within the range of 1.5-4:1). Assuming LABS to be 95% biodegradable, the ratio between the total nonbiodegradable and biodegradable surfactants disposed in Israel municipal wastewaters is approximately 1:6, i.e. (16.3 [Table I] × 63.6 [Table II]) + (83.7 [Table I] × 5 [Table II])/83.7 [Table I] × 95 + 16.3 [Table I] × 36.4 [Table II].

The importance of the study of surfactant biodegradation under realistic conditions has been stressed recently (4,8,17), particularly with respect to "hard" nonionics of the branched-chain alkylphenol-based ethoxylates, the biodegradation of which is highly temperature dependent (18).

Typical curves of primary degradation of both anionic and nonionic surfactants in our municipal wastewaters under semi "in vivo" conditions (i.e. no treatment of any kind, leaving the hydraulic residence time—HRT—to become the dominant factor) are illustrated in Figure 1.

Significantly, we find that the extent of primary degradation of both anionic and nonionic surfactants is about

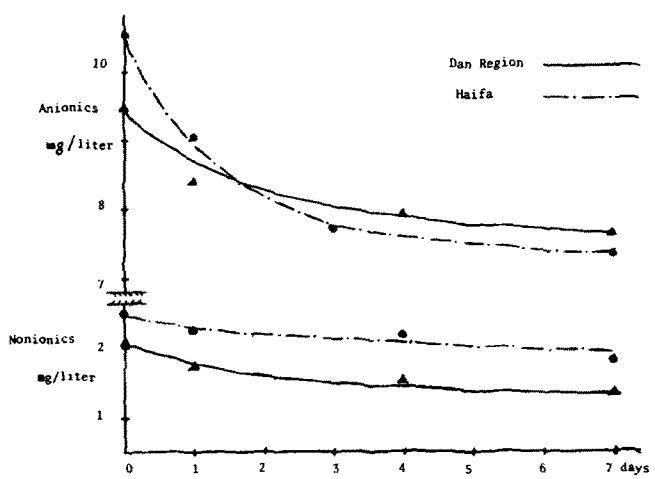

FIG. 1. Typical curves of primary degradation of anionic and nonionic surfactants in Israeli municipal wastewaters (semi in vivo conditions).

TABLE III

Typical Concentrations[a] of Anionic and Nonionic Surfactants in Representative Municipal Wastewater Effluents[b] in Israel (Summer 1983)

Location of sewage	Anionic surfactants	Nonionic surfactants	Total	Anionic/nonionic ratio (%)
Tel Aviv (north)[d]	11.0	2.15	13.15	83.6:16.4
Dan Region[e]	0.3	0.45	0.75	40.0:60.0
Haifa[f]	0.7	0.25	0.95	73.7:26.3
Hadera[f]	1.3	0.3	1.6	81.3:18.7
Tiberias (lower)[g]	4.3	0.4	4.7	91.5: 8.5
Average[c]	5.8	1.25	7.05	82.3:17.7

[a,b,c]Same as in Table I.

[d]Untreated effluents.

[e]Extensive primary-secondary treatment.

[f]The treatment includes precipitation ponds followed by aerated oxidation ponds.

[g]Primary treatment consisting only of precipitation ponds.

TABLE IV

Removal of Surfactants—via Biodegradation and/or Treatment in Representative Municipal Wastewaters in Israel[a] (Summer 1983)

Location of sewage	Influent[b]		Effluent				Actual surfactant removal (%)		
			Predicted		Actually found				
	Anionic	Nonionic	Anionic	Nonionic	Anionic	Nonionic	Anionic	Nonionic	Total
Dan Region	11.2	2.35	1.1[c]	1.5[d]	0.3	0.45	97.3	80.8	94.4
Haifa	9.2	1.2	7.8[e]	1.1[e]	0.7	0.25	94.4	79.2	92.6
Tel Aviv (north)	11.0	2.2	11.0[f]	11.0[f]	11.0[f]	2.2[f]	0	0	0
Average	10.7	2.05	7.6	1.8	5.9	1.3	44.9	36.6	43.6

[a]Figures are mg/liter.

[b]Total volume of wastewaters on the three given sites (8, 6 and 15 X 10^4 respectively) is 29 X 10^4 cubic meters per 24 hr (more than 50% of the total amount of municipal wastewater in the country).

[c]Assuming >90% biodegradation under optimal conditions.

[d]Based on the nonbiodegradable-biodegradable ratio (63.3:36.4) of nonionic surfactants (Table I).

[e]Based on the extent of biodegradation per 24 hr found previously under semi "in vivo" conditions.

[f]Direct discharge (into the Mediterranean Sea) without any treatment.

20% during a one-week period. This result suggests what one should expect concerning surfactant biodegradation in municipal wastewaters receiving no treatment.

Table III summarizes data regarding the concentrations of surfactants found in municipal wastewater effluents untreated or after various kinds of treatments.

Obviously, the more sophisticated the treatment process, the lower the surfactant concentrations remain in the effluents. Similarly, the anionic-nonionic ratio changes in favor of the nonionic surfactants (compared with the ratio in the influents in Table I). This is to be expected because the anionic detergents are essentially biodegradable, whereas about 2/3 of the nonionic surfactants are nonbiodegradable (Table II), and the percentage of removal of both types is comparable in conventional sewage treatment processes (5).

The actual extent of surfactant removal in the three largest municipal sewage sites in the country is given in Table IV. As can be seen, appropriate treatment effectively removes about 95% of the practically biodegradable anionic surfactants present in our municipal wastewaters. The extent of nonionic surfactant removal from municipal wastewater influents is around 80%.

Clearly, the presence of nonbiodegradable nonionic surfactants in our municipal wastewaters (and their share in the Israeli detergent market to begin with) contributes to this state of affairs.

In the other Western industrial countries, there is a clear switch to biodegradable nonionic surfactants at the expense of both the anionic LABS and the nonbiodegradable ethoxylated branched chain alkylphenols and alcohols (7,14).

In view of the expected increase in the use of both surfactants and reclaimed sewage water, particularly for unlimited agricultural purposes, the monitoring of wastewaters with respect to their detergent content, biodegradability and type distribution is clearly imperative.

This study may serve as a "first approximation" model and a basis for rational decision making for action concerning the production, use and disposal of surfactants.

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♣A Comparison of Conventional and in situ Methods of Transesterification of Seed Oil from a Series of Sunflower Cultivars

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ABSTRACT

The cost of vegetable oil monoesters represents one of the major restrictions on their use as an alternative fuel for diesel engines. This cost can be reduced by increasing the yield of esters produced from a given quantity of oilseed.

Transesterification of sunflowerseed oil in situ with acidified methanol has been shown to produce fatty acid methyl esters in yields significantly greater than those obtained from conventional reaction with pre-extracted seed oil. Yield improvements of over 20% were achieved and could be related to the moisture content of the seed. Fatty ester compositions and cloud points of the products from the in situ reactions were virtually identical to those of esters produced using conventional techniques.

INTRODUCTION

In many parts of the world considerable interest has been focused over recent years on the possibility of using vegetable seed oils and their derivatives as extenders of, or replacements for, conventional distillate as a fuel for diesel engines. The Australian position has been described by Stewart et al. (1). From the numerous reports which have appeared, it has become apparent that most seed oils and their monoesters, formed by transesterification with simple aliphatic alcohols, are capable of performing very satisfactorily in a diesel engine, particularly over the short to medium term. Some problems associated with longer term running have been identified with and attributed to the high viscosity of the vegetable oils (typically 10 times that of distillate) and to the high degree of unsaturation of the fatty acids of some candidate oils (e.g. linseed).

However, it is perhaps not in the area of performance, but in that of economics, where the widespread use of such an alternative fuel has its greatest impediment. Consequently, it is of the utmost importance that seeds of high oil content are considered and that processing efficiencies are maximized. It is to the improvement of processing efficiency that the present paper is addressed.

Bruwer and his colleagues (2) suspected that the high viscosity of sunflowerseed oil detracted from its effectiveness as a diesel fuel substitute; they introduced the practice of converting the raw oil to its methyl or ethyl monoesters by the relatively simple process of alkali-catalyzed transesterification. These simple esters of sunflower oil were of a viscosity approaching that of conventional distillate and performed well in dynamometer tests with tractor engines.

Transesterification of vegetable seed oil is conventionally carried out by subjecting the pre-extracted oil to treatment with the appropriate alcohol, in the presence of an acid or alkaline catalyst.

The concept of transesterification of sunflowerseed oil in situ was described in an earlier report (3), and it was demonstrated there that significant increases in ester yields could be achieved by such a method. At that time, little data were presented concerning the qualitative nature of the esterified products. It is of obvious importance that the products obtained by in situ reaction be at least as suitable as a diesel fuel substitute as those derived from the conventional treatment of the oil and do not detract from this suitability by, for example, introducing more oxygenated species, increasing viscosity or raising the fuel cloud point.

This paper describes results obtained from the transesterification in situ of seed oil from a series of sunflower cultivars grown under the influence of different temperature regimes, and compares these results with those obtained from conventional transesterification of the pre-extracted oil.

EXPERIMENTAL

Sunflower Seeds

Seeds were from sunflower cultivars Suncross 150 and Hysun 31, grown in an artificially controlled environment under the influence of a range of temperature regimes. Seed moisture and oil contents were evaluated and are tabulated in the next section.

Thin Layer Chromatography (TLC)

Thin layer chromatography was performed on glass plates coated with silica gel HF254 (Merck). The developing solvent was petroleum ether, diethyl ether and acetic acid (85:15:1, v/v/v). Iodine vapor was used for visualization.

Gas Liquid Chromatography (GLC)

Gas liquid chromatography was carried out on a Pye Series 104 Gas Chromatograph equipped with a flame ionization detector, using nitrogen as carrier gas. Separation of the fatty acid methyl esters was accomplished using a glass

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