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Fuel Alcohol Extraction Technology Commercialization Conference

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FUEL ALCOHOL EXTRACTION TECHNOLOGY COMMERCIALIZATION CONFERENCE

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Summary

The *fualex*, or *fu*el *al*cohol *ex*traction process, uses a combination of hydrocarbon and surfactant to remove neutral solvents, such as butanol, ethanol, isopropanol, and acetone, from aqueous solution. The hydrocarbon extractants use may be fuels, such as gasoline, furnace oil, and diesel fuel. Surfactant concentrations ranging from 1 to 10 g/liter and hydrocarbon ranging from 0.01 to 1 liter per liter aqueous alcohols solution have been investigated. The *fualex* process was tested on solutions which contain 5% w/v total neutral solvents, since this is near maximum for the fermentation product stream. The neutral solvents are removed in the form of an emulsion which is white to light bluish in the visible range. The emulsion has potential for direct use in fuels or as an intermediate for obtaining purified solvents.

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1. Introduction

There is increasing interest in the use of alcohols in fuels. Ethanol in gasoline is a primary focus of attention; however, other alcohols, including methanol, isopropanol, and butanol also are being considered for fuel use. Net ethanol energy production is uncertain. Distillation and dewatering consume much of the energy required to use ethanol in motor fuel. We have been interested in a method which may decrease the energy required to produce alcohols, particularly 1-butanol and 2-propanol, for use in either fuels or enhanced oil recovery.

ENHANCED OIL RECOVERY

Estimates of chemicals required for the production of one barrel of incremental oil by micellar flooding vary depending upon the reservoir and oil recovered, but are often on the order of one to two lb of high viscosity polymer, seven to 20 lb surfactant, and two to seven lb higher alcohols. Although production and injection of the chemicals required uses only a small fraction of the energy in the recovered oil, production of these chemicals from sources other than petroleum feedstocks, particularly renewable resources, would be desirable. Present national production of the alcohols required would not support over one million barrels per day even if completely devoted to oil recovery. One million barrels per day is only about 7% of the present U.S. oil consumption.

If micellar flooding is implemented on a major scale, the need for new chemical production facilities will provide an opportunity for use of more efficient processes. It will also encourage evaluation of production methods currently in use. For example, distillation of a neutral solvents stream can produce relatively pure product streams of butanol, 2-propanol, ethanol, and acetone. Tests performed by Amoco Research indicate that 1) separation of the solvents from one another may not be necessary for use in enhanced oil recovery and 2) dewatering of the mixture past the separation from water which occurs due to butanol immiscibility may not be necessary. Lowering the product purity requirements decreases production energy.

FUEL USE

Fermentations which produce 1-butanol, 2-propanol, and ethanol have been used on a commercial scale in Taiwan (Prescott and Dunn 1959), and *Clostridia* which perform such fermentations are available from culture collections, such as that of the Northern Regional Research Laboratory in Peoria, Illinois. Several advantages of a predominantly 1-butanol and 2-propanol mixture for use in fuels exist: these alcohols have a higher fuel value than does ethanol; phase separation between hydrocarbon and water is lessened over ethanol systems; and safeguarding of product during production does not involve the burdensome legal problems posed by ethanol.

Patent literature indicates that mixtures which contain water, surfactant, and gasoline or diesel fuels which are in the form of a microemulsion are stable for long periods of time over a broad range of temperatures without major increases in fuel viscosity. (Piotrowski 1977 and Wenzl and Steinmann 1978). Microemulsion fuels were tested by the Army and found to have improved safety characteristics, in addition to decreased diesel emissions of particulates and oxides of nitrogen, under many circumstances (Owens and Wright 1976). These indicate that dewatering of high concentra-

tion alcohols prior to fuel use may not be necessary if proper fuel additives are chosen.

WHY FUALEX ?

The *Fualex*, or *Fu*el *al*cohols *ex*traction process, can be used to provide a mixture suitable for use in either fuels or enhanced oil recovery. A small amount of a surfactant and a hydrocarbon, such as gasoline or diesel fuel, is added to a fermentation broth containing alcohols. If the surfactant and hydrocarbon are correctly matched to each other and to the alcohols mixture, an emulsion is formed as a third layer between the hydrocarbon and the aqueous layer. This third layer is enriched in alcohols which were in the fermentation broth, and may be removed. The process can be repeated or can be performed continuously to provide the required alcohols removal, and is applicable to mixtures which contain ketones also. Based on patent literature, it should be possible to incorporate the emulsion or microemulsion into fuels. These microemulsion systems appear similar in some respects to micellar flood systems and evaluation of them for oil displacement appears potentially profitable.

The *Fualex* process requires little energy compared to conventional ethanol dewatering for use in fuels, and most of the surfactants used to date have exceptionally low toxicity. Some of the materials tested are marketed as gasoline or diesel fuel additives, and they are major bulk chemicals.

2. Neutral Solvents Fermentations

Neutral solvents blends are mixtures of 1-butanol, 2-propanol, ethanol, and acetone. Although ethanol produced by yeast fermentation and methanol produced by pyrolysis and synthesis from biomass derived gases are being currently considered for use in fuel blends, neutral solvent mixtures produced by bacteria, generally *Clostridia*, are also suitable for this use. Core flood data from our micellar flood involvement indicate that the solvent mixtures produced by these organisms may also be suitable for direct use as cosurfactants in micellar flooding, as opposed to ethanol or methanol. Additionally, neutral solvents blends, which are predominantly 1-butanol, added to hydrocarbons dissolve more water than do ethanol or methanol blends with hydrocarbon. This property lessens difficulties in storage and in use of motor fuels. The heats of combustion of 1-butanol and 2-propanol are also higher than those of ethanol and methanol.

Original work in neutral solvents production started just before World War I, and the solvents produced were used mainly for war materials manufacture. The process used a grain feedstock, often barley based. Process use was restricted until World War II and the subsequent Korean conflict, when it was again revived for producing war materials such as cordite, varnishes, rubber, and penicillin. Both corn and molasses were used as feedstocks, and much of the fermentation was performed in Cuba. When nationalization removed the Cuban facilities from U.S. control, production from petroleum became the preferred method of butanol production. Some of the cultures used were stored in culture collections; however, it is important to remember that the cultures were designed for different feedstocks and conditions than those which might be best used today.

A comparison of neutral solvents versus ethanol production shown in Table 2.1 indicates some of the advantages and difficulties inherent in neutral solvents fermentations as compared to ethanol fermentations. Although the total energy of the fermentation products and the distiller's dry solids from neutral solvents is higher, the produced solvent concentration is presently lower and thereby, for a given capacity the required fermenter volume greater, since the fermentations take roughly equivalent times. Molasses was chosen for the comparison because more reliable production figures are available for this substrate; however, there is an additional advantage in the easier production of neutral solvents from grains: no prehydrolysis is generally required because the organisms have the ability to break down complex carbohydrates, and yeasts generally do not. We picked operating data from the 1950's because it permitted comparison of the two processes from full scale plant data, rather than estimates from bench scale work, which are often overoptimistic.

Table 2.1. Comparison of ethanol and neutral solvents production.

Material	*Ethanol*		*Neutral Solvents*	
	Amount, kg	10^6 cal	Amount, kg	10^6 cal
		Input		
Molasses	1,000		1,000	
H_2O	1,430		9,420	
Mash Volume, liters	2,020		9,500	
		Output		
CO_2	186		321	
H_2			8	0.14
DDS[a]	155		286	
1-Butanol			115	0.99
Acetone			49	0.36
Ethanol	194	1.38	5	0.04
Total		1.38		1.53

[a]DDS = Distillers' dried solids.
Adapted from Prescott and Dunn 1959.

3. Fuel Microemulsions

Microemulsions are very fine emulsions, well less than 1 μm, and often characterized as 0.05 to 0.1 μm, in diameter, which are stable for long periods of time and over a wide range of temperature. In the *Fualex* process, alcohols are removed from solution as a part of macroemulsions. If these are to be used in fuel a blend which contains hydrocarbons, alcohols, and water as well is needed. Such blends have been claimed in patents, and a body of work concerned with the improved combustion characteristics of these blended fuels and of mechanically emulsified fuels is available. There is also work on microemulsions in enhanced oil recovery, which is briefly described.

FUELS LITERATURE

Early work by the U.S. Army was motivated by the desirability of less explosive fuels for combat vehicles. The Army Fuels and Lubricants Laboratory determined that derivatives of common vegetable and tall oil constituents, could be added to diesel fuel together with water and emulsified with the production of a suitable fuel (Owens and Wright 1976). The derivatives used included an alditol ethoxylated fatty acid. The energy content of the fuel decreased with increasing water content. However, surprisingly, these researchers found that they obtained a decrease of nearly 15% in oxides of nitrogen and smoke opacity, or particulates, using a 5% water emulsion stabilized with a surfactant blend having a hydrophile-lipophile balance, *HLB*, of 5.4. Using this mixture, carbon monoxide emissions increased slightly, and unburned hydrocarbons increased substantially. With addition of 10% water, cetane number of the fuel decreased from 48 to 43.

Continued research the Army Fuels and Luricants Research Laboratory (Wetherfor *et al* 1979) indicated that the water diesel fuel blends of concentrations less than 10% did not result in significant losses of engine power at constant diesel fuel rates in unmodified LDT-465-1C diesel engines. These blends had significant fire-resistant properties which made them attractive candidates for reducing combat related fuel fires. However, a thorough investigation of the relationship between surfactant-water-fuel should be made, especially in the light of the Army's commitment to increasing use of these fuels. The tests involved continuous use of full scale equipment for several months. The evolved fire resistant fuels have changed to to an ethanolamine based oleate detergent and use higher detergent and antimist agent concentrations. The only major problems with the fire-resistant fuel arose from a materials incompatibility with urethane. The surfactant in the fuel serves as an effective biocide. These recommendations will probably make a water-in-diesel-fuel emulsion the standard military combat fuel by the mid-1980's, as was recommended.

Storment and Coon investigated the combustion of unstabilized water in fuel emulsions in a single cylinder diesel engine. Their results are similar to those of Owens and Wright in that they also obtained significant decreases in oxides of nitrogen, ranging to 60% in some cases, and in smoke production, ranging up to 70%. A corresponding increase in unburned hydrocarbon emissions was found by both investigators. Major differences between the large engine tests and the single cylinder engine tests were in fuel consumption, where Storment and Coon found slight, but statistically signifi-

cant, decreases in fuel consumption, and in carbon monoxide emissions, where both increase and decrease were found, depending upon conditions tested. As with Owens and Wright, no problems in engine operation were encountered, although fuel water contents ranged up to 23%. Similar results were obtained with a marine configured Detroit Diesel 6-71 engine mounted on a dynamometer test stand (Walter 1978).

Dryer and Glassman (1977) investigated fundamental aspects of emulsified fuel combustion. They found that additions of alcohols as large as decanol improved droplet size distribution from injectors, and, to a large extent, confirmed the work of Owens and Wright and Storment and Coon. They evaluated uses for diesel and gasoline fuels which contain water in emulsion. They contended that power generation was a good choice for short term applications in that major reductions in emissions could be obtained without significant decreases in power output or significant emissions control costs. Safety was also a major concern in their research, due to interest from the military and from several industries, such as coal mining and utilities. A major contribution of this project was the determination that gas turbine engine emissions could, like those of diesel and standard automotive engines, be sharply reduced with microemulsified water in fuel blends.

Cinematographic studies of combustion taken by Dryer and Glassman indicated that an emulsion having 0.1 to 5 μm droplet sizes provided the best combustion. This is in the range between a very fine emulsion and a microemulsion.

PATENT LITERATURE

The most comprehensive treatment of microemulsion fuel compositions is Wenzl and Steinmann (1978). These inventors covered production of thermally stable diesel and gasoline fuels containing water using fatty acids, their salts, a variety of ethoxylated surfactants, and water soluble alcohols. Alcohols as large as cyclohexanol were used. The resultant microemulsions were quite stable, with unleaded gasoline mixtures clear and fluid at -24 C, and most diesel fuel mixtures clear at -5 C. The mixtures were gently hand stirred to produce clear, stable solutions, as opposed to the work reported by Owens and Wright where high shear mixing devices were used.

A second patent in this area by Piotrowski (1978) has issued. He claims a motor fuel in the form of a microemulsion which is a mixture of gasoline, methanol, and water and a surfactant having a hydrophile-lipophile balance of 3 to 4.5. He was also able to produce a clear, stable solution by stirring, and his chemical composition, like that of AFLRL, contains amines.

ENHANCED OIL USES

A comprehensive review article on this subject by Shah *et al* (1977) indicates that there are many similarities between fuels work and that in enhanced oil recovery. However, the article indicated that higher levels of surfactants and coagent alcohols are generally used in enhanced oil recovery systems than in fuel applications.

PRACTICAL IMPLICATIONS

It appears that it is possible to produce stable microemulsions from mixtures of fuels, water, alcohols, and appropriate surface active agents. Such fuels are reported to have improved combustion and safety characteristics, even at water contents of 10%. We have used surface active agents from the groups of polyoxyethylene derivatives as a part of this work, and are inclined to feel that dewatering of the alcohol - surfactant - fuel emulsion prior to fuel use may not be necessary.

4. Surfactant Structure and Properties

Fualex is concerned with the extraction of alcohols and ketones from aqueous solution into hydrocarbon mixtures through the addition of a surfactant, usually a a polyoxyalkylene polymer and a small amount of hydrocarbon. A resultant mixture consisting of hydrocarbon, alcohol(s) or ketone(s), polyoxyalkylene polymer, and water, can be directly added to fuels or further purified. Where the polyoxyalkylene polymer - alcohol - ketone combination is suitable for use in enhanced oil recovery, it may be possible to use the mixture directly for injection. Surfactant structure and prior art in surfactant manufacture is discussed below.

POLYOXYALKYLENE POLYMERS

These polymers consist of repeating units of oxylated alkanes, such as ethylene oxide, propylene oxide, and butylene oxide. Both randomly polymerized and block polymers are available, and the polymers have different substituents and end groups, depending on manufacturer and intended use. They are widely used in applications, such as emulsification, foam control, and cleaning compounds, where surface and interfacial tension modification is required. Some are also being considered for use in tertiary oil recovery as surfactants which reduce interfacial tension between oil-in-place and water. These materials have been made for decades and the patent literature is extensive; however, we will cite patents covering the groups of material which we have used where we have been able to obtain such information from the manufacturer or from literature. Much of the information on polymer chain length has been kindly provided by the manufacturers of the products used, and we have assumed their information to be correct.

Polymers of Polyoxyethylene and Polyoxypropylene

Fig. 4.1 shows a structure which consists of alternating blocks of polyoxyethylene, polyoxypropylene, and polyoxyethylene. This structure is used by BASF-Wyandotte in their *Pluronic* series, and is covered by U.S. patent 2,676,619 (Lundsted 1954). The molecules are a cogeneric mixture of conjugated polyoxypropylene-poly oxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups, and an organic radical having a molecular weight of less than 200. The compounds are characterized by having all of the oxyethylene in polyoxyethylene blocks and all of the oxypropylene in polyoxypropylene blocks. Lundsted claimed mixtures in which the average molecular weight of the polyoxypropylene polymers in mixture were at least 900, as determined by the hydroxyl number and the oxyethylene groups present were 20 to 90%, by weight, of the mixture.

As shown in Table 4.1, we have covered a range of these materials which goes from an average of 1.25 repeating groups of oxyethylene to nearly 100 repeating groups, and from 0 to 70 repeating groups of oxypropylene. The molecular weights of the polymers range from 200 to 12,500. All of the samples tested did, so far as we know, have hydrogen end caps on the polymeric chains; however, as indicated in the references below, end caps can contain, among other things, hydrogen, alkane, alkene, acyl, and aryl groups. The structures ranged

$$R_1\ (OH_4C_2)_{x_1} - O - (C_3H_6O)_{y_1} - (C_2H_4O)_{x_2}\ R_2$$

Fig. 4.1. Polyoxyethylene - polyoxypropylene - polyoxyethylene polymers.

Table 4.1. Polyoxyethylene - polyoxypropylene - polyoxyethylene polymers.

Designation	Manufacuturer	Approximate molecular wt	Fraction hydrophile	x_1	x_2	y_1	R_1	R_2
P2000	Dow	2000	0.00	0.	0.	34.5	H	H
P4000	Dow	4000	0.00	0.	0.	69.0	H	H
L31	BASF-W	1100	0.10	1.3	1.3	17.1	H	H
L61	BASF-W	2000	0.10	2.3	2.3	31.0	H	H
L81	BASF-W	2750	0.10	3.1	3.1	42.7	H	H
L121	BASF-W	4400	0.10	5.0	5.0	68.3	H	H
L42	BASF-W	1630	0.20	3.7	3.7	22.5	H	H
L62	BASF-W	2500	0.20	5.7	5.7	34.5	H	H
L72	BASF-W	2759	0.20	6.3	6.3	37.9	H	H
L122	BASF-W	5000	0.20	11.4	11.4	69.0	H	H
P103	BASF-W	4950	0.30	16.9	16.9	59.8	H	H
P123	BASF-W	5750	0.30	19.6	19.6	69.4	H	H
L44	BASF-W	2200	0.40	10.0	10.0	22.8	H	H
L64	BASF-W	2900	0.40	13.2	13.2	30.0	H	H
P94	BASF-W	5100	0.40	23.2	23.2	52.8	H	H
P104	BASF-W	5850	0.40	26.6	26.6	60.5	H	H
L35	BASF-W	1900	0.50	10.8	10.8	14.7	H	H
P75	BASF-W	4150	0.50	23.6	23.6	35.8	H	H
P105	BASF-W	6500	0.50	36.9	36.9	56.0	H	H
F77	BASF-W	6600	0.70	52.5	52.5	34.1	H	H
F87	BASF-W	7700	0.70	61.3	61.3	39.8	H	H
F127	BASF-W	12500	0.70	99.4	99.4	64.7	H	H
E200	Dow	200	1.00	4.5	0.	0.	H	H
E400	Dow	400	1.00	9.1	0.	0.	H	H
E600	Dow	600	1.00	13.6	0.	0.	H	H
E1000	Dow	1000	1.00	22.7	0.	0.	H	H
E1450	Dow	1450	1.00	33.0	0.	0.	H	H
E4000	Dow	4000	1.00	90.9	0.	0.	H	H
E8000	Dow	8000	1.00	181.8	0.	0.	H	H

from 0 to 100% by weight of ethylene oxide hydrophile.

Fig. 4.2 shows a structure which consists of alternating blocks of polyoxypropylene, polyoxyethylene, and polyoxypropylene. This structure is used by BASF-Wyandotte in their *Pluronic R* series, and is covered by U.S. patent 3,036,118 (Jackson and Lunsted 1962). This structure is similar to that of Fig. 4.1 except that the positions of the oxyethylene and oxypropylene chain groups are reversed. As with the polyoxyethylene - polyoxypropylene - polyoxyethylene structure, Jackson and Lundsted claimed mixtures in which the average molecular weight of the polyoxypropylene polymers in the mixture were at least 900, and the oxyethy-

$$R_1\ (OC_3H_6)_{y_1} - O - (C_2H_4O)_{x_1} - (C_3H_6O)_{y_2}\ R_2$$

Fig. 4.2. Polyoxypropylene - polyoxyethylene - polyoxypropylene polymers.

lene groups in the mixture constituted from about 20 to about 90 weight percent of the mixture. An upper limit in average molecular weight of the polymers around 25,000 was a part of the claim.

The materials from this groups which are shown in Table 4.2 range from averages of 7.6 to 23.4 polyoxypropylene groups, and from 14.2 to 163.6 polyoxyethylene repeating groups. The lowest average molecular weight is 1970, and the highest, 9000. All of the end caps are hydrogens, but, as mentioned earlier, this may be substituted by many materials. The only manufacturer was BASF-Wyandotte. As can be seen from the brief description of U.S. 3,036,118, the range of available materials covered under the patent is considerably larger.

Fig. 4.3 shows a branched structure marketed by BASF-Wyandotte as a standard *Tetronic* and manufactured under U.S. patent 2,979,528 (Lundsted 1961). The patent claims a number of central structures, including ammonia, primary alkyl amines, alkylene polyamines, alkanolamines, piperazine, and carbon substituted alkylpiperazines, hydroxylamine and aminophenol, the structure of the compounds being such that all of the oxypropylene groups are present in oxypropylene chains attached to the reactive hydrogen atoms, and all of the oxyethylene groups are present in oxyethylene chains attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 900 ranging to about 25,000 and the oxyethylene groups constituting 20 to 90 weight percent of the mixture of compounds. Industrial usage currently favors the Fig. 4.3 structure, which, according to claim 4, uses a central alkylene polyamine.

The materials shown in Table 4.3 range from 10 to 80% polyoxyethylene in weight, and contain average chain lengths of 1.9 to 124.7 repeating polyoxyethylene groups, assuming that all four such chains are equal

Table 4.2. Polyoxypropylene - polyoxyethylene - polyoxypropylene polymers.

Designation	Manufacuturer	Approximate molecular wt	Fraction hydrophile	x_1	y_1	y_2	R_1	R_2
25R2	BASF-W	3120	0.20	14.2	21.6	21.6	H	H
31R2	BASF-W	3400	0.20	15.5	23.4	23.4	H	H
17R4	BASF-W	2700	0.40	24.5	14.0	14.0	H	H
31R4	BASF-W	4300	0.40	39.1	22.0	22.0	H	H
10R5	BASF-W	1970	0.50	20.1	7.6	7.6	H	H
25R5	BASF-W	5000	0.50	56.8	21.6	21.6	H	H
17R8	BASF-W	7500	0.80	136.4	12.9	12.9	H	H
25R8	BASF-W	9000	0.80	163.6	15.5	15.5	H	H

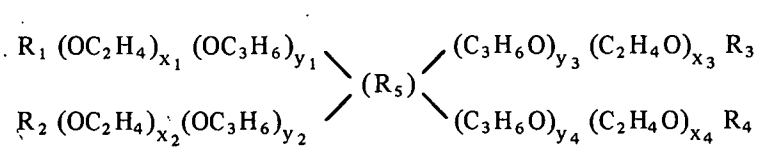

Fig. 4.3. Hydrophile out *Tetronic* manufactured by BASF-Wyandotte.

in length. The polyoxypropylene blocks range from 4.1 to 32.2 repeating units, again assuming equal length. The central groups is ethylene diamine. End caps are hydrogen, although this may be varied. Average molecular weights range from 1650 to 27,500.

Fig. 4.4 shows a branched structure marketed by BASF-Wyandotte as a *Tetronic-R* and manufactured under U.S. patent 3,036,118. This material is similar to that shown in Fig. 4.3, but the relative position of the polyoxyethylene and polyoxypropylene groups is reversed.

The materials shown in Table 4.4 range from 20 to 40% polyoxyethylene in weights and contain average chain length of 1.3 to 28.3 oxyethylene groups and 4.1 to 32.2 oxypropylene groups. The central group is ethylene diamine. End caps are hydrogen, although this may be varied. Average molecular weight ranges between 1240 and 12,500.

Polyoxyethylene - Alkane Esters

Fig. 4.5 indicates the general structure of an ethoxylated alkane or alkene acid. The materials which we used were made by three manufacturers, Armak, Emery, and ICI Americas, although many other companies make these materials. It is also possible to use other polyoxyalkanes than polyoxyethylene, either singly, in block groups like the *Pluronics*, or in mixed chains.

The materials in Table 4.5 range from 4 to 23 oxyethylene groups, and from molecular weights of 462 to 1298. Members contain 1 and 2 acid esters, with hydrogen as the end cap where no ester is used. The weight

Table 4.3. BASF-Wyandotte *Tetronic* surfactant.

Designation	Approximate molecular wt	Fraction hydrophile	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	R_1	R_2	R_3	R_4	R_5
T701	3400	0.10	1.9	1.9	1.9	1.9	13.0	13.0	13.0	13.0	H	H	H	H	$>NCH_2CH_2N<$
T901	4750	0.10	2.7	2.7	2.7	2.7	18.2	18.2	18.2	18.2	H	H	H	H	$>NCH_2CH_2N<$
T1101	5600	0.10	3.1	3.1	3.1	3.1	21.5	21.5	21.5	21.5	H	H	H	H	$>NCH_2CH_2N<$
T1301	6800	0.10	3.8	3.8	3.8	3.8	26.1	26.1	26.1	26.1	H	H	H	H	$>NCH_2CH_2N<$
T1501	7900	0.10	4.5	4.5	4.5	4.5	30.4	30.4	30.4	30.4	H	H	H	H	$>NCH_2CH_2N<$
T304	1650	0.40	3.6	3.6	3.6	3.6	4.1	4.1	4.1	4.1	H	H	H	H	$>NCH_2CH_2N<$
T504	3400	0.40	7.6	7.6	7.6	7.6	8.6	8.6	8.6	8.6	H	H	H	H	$>NCH_2CH_2N<$
T704	5500	0.40	12.4	12.4	12.4	12.4	14.1	14.1	14.1	14.1	H	H	H	H	$>NCH_2CH_2N<$
T904	7500	0.40	16.9	16.9	16.9	16.9	19.2	19.2	19.2	19.2	H	H	H	H	$>NCH_2CH_2N<$
T1104	8300	0.40	18.7	18.7	18.7	18.7	21.3	21.3	21.3	21.3	H	H	H	H	$>NCH_2CH_2N<$
T1304	10500	0.40	23.7	23.7	23.7	23.7	27.0	27.0	27.0	27.0	H	H	H	H	$>NCH_2CH_2N<$
T1504	12500	0.40	28.3	"28.3	28.3	28.3	32.2	32.2	32.2	32.2	H	H	H	H	$>NCH_2CH_2N<$
T707	12000	0.40	47.5	47.5	47.5	47.5	15.4	15.4	15.4	15.4	H	H	H	H	$>NCH_2CH_2N<$
T1107	14500	0.40	57.4	57.4	57.4	57.4	18.7	18.7	18.7	18.7	H	H	H	H	$>NCH_2CH_2N<$
T1307	18600	0.40	73.7	73.7	73.7	73.7	24.0	24.0	24.0	24.0	H	H	H	H	$>NCH_2CH_2N<$
T1508	27500	0.80	124.7	124.7	124.7	124.7	23.7	23.7	23.7	23.7	H	H	H	H	$>NCH_2CH_2N<$

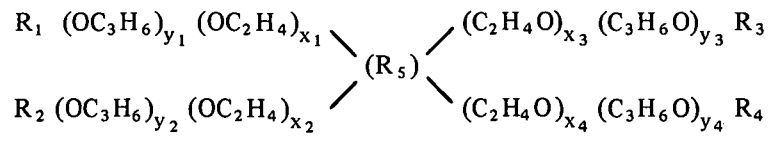

Fig. 4.4. Hydrophobe out *Tetronic* manufactured by BASF-Wyandotte.

Table 4.4. BASF-Wyandotte *Tetronic-R* surfactant.

Designation	Approximate molecular wt	Fraction hydrophile	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	R_1	R_2	R_3	R_4	R_5
T30R2	1240	0.20	1.3	1.3	1.3	1.3	4.1	4.1	4.1	4.1	H	H	H	H	$>NCH_2CH_2N<$
T50R4	3400	0.40	7.6	7.6	7.6	7.6	8.6	8.6	8.6	8.6	H	H	H	H	$>NCH_2CH_2N<$
T70R4	5500	0.40	12.4	12.4	12.4	12.4	14:1	14.1	14.1	14.1	H	H	H	H	$>NCH_2CH_2N<$
T90R4	7500	0.40	16.9	16.9	16.9	16.9	19.2	19.2	19.2	19.2	H	H	H	H	$>NCH_2CH_2N<$
T150R4	12500	0.40	28.3	28.3	28.3	28.3	32.2	32.2	32.2	32.2	H	H	H	H	$>NCH_2CH_2N<$

Table 4.5. Ethoxylated alkane and alkene acid.

Designation	Manufacturer	Approximate molecular wt	Fraction hydrophile	x_1	R_1	R_2
ISA-4	Emery	462	0.38	4.	$C_{17}H_{35}CO$	H
P200DO	Armak	768	0.26	4.5	$C_{17}H_{c5}CO$	$C_{17}H_{35}CO$
P200DL	Armak	770	0.26	4.5	$C_{17}H_{35}CO$	$C_{17}H_{33}CO$
P400DO	Armak	970	0.41	9.1	$C_{17}H_{33}CO$	$C_{17}H_{35}CO$
60/15	Armak	506	0.44	5.0	$C_{17}H_{c5}CO$	H
SA-7	Emery	594	0.51	7.0	$C_{17}H_{35}CO$	H
OA-7	Emery	592	0.52	7.0	$C_{17}H_{33}CO$	H
SA-8	Emery	638	0.55	8.0	$C_{17}H_{35}CO$	H
ISA-9	Emery	682.	0:59	9.0	$C_{17}H_{35}CO$	H
P400MO	Armak	684	0.59	9.0	$C_{17}H_{33}CO$	H
60/20	Armak	726	0.61	10.0	$C_{17}H_{35}CO$	H
OA-10	Emery	724	0.61	10.0	$C_{17}H_{33}CO$	H
RE22	ICI-Am	820	0.65	12.0	tall acids[a]	H
242/25	Armak	952	0.69	15.0	tall acids[a]	H
RE20	ICI-Am	996	0.71	16.0	tall acids[a]	H
SA-23	Emery	1298	0.78	23.0	$C_{17}H_{35}CO$	H

[a]Tall oil acids contain approximately: 24% oleic acid, 19% linoleic acid, 4% conjugated linoleic acid, 14% abietic acid, 7% neoabietic acid, 26% related rosin acids, and 6% other materials.

$$R_1-O-(C_2H_4O)_{x_1}\ R_2$$

Fig. 4.5. Ethoxylated alkane or alkene acid.

percent hydrophile ranges from 26 to 78. Both saturated and unsaturated acids have been used in various members of the group. Both single acids and mixed acid groups are present, and some of the acids, abietic, neoabietic, and rosin acids, in the mixed acid tall oil components are contain aromatic rings. As with previous examples, it is possible to use other materials than hydrogen as end caps, and various manufacturers do so.

Fatty Acid Derived Amine Ethoxylate

Fig. 4.6 shows a fatty acid derived amine ethoxylate. This material has a fatty acid

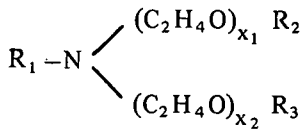

Fig. 4.6. Ethoxylated fatty acid amine.

derived amine center and polyoxyethylene side branches. As with most of the ethoxylated polymers, the end caps can be varied.

As shown in Table 4.6, the compound tested, Ethomeen 0/15, has an approximate molecular weight of 487 and is 48.5% hydrophile. It has an average of 2.5 repeating groups of oxyethylene per chain on the two chains, and both chains have hydrogen end caps. The alkane tail is has 18 carbons and 35 hydrogens, and is saturated. Many variations also exist for this general type of structure, and common ones may include alkane and oxyethylene chain lengths and chain end caps.

Polyoxyalkylene - Polyol Ethers

Fig. 4.7 shows a triol with mixed polyoxyalkylene chains, as manufactured by Dow. Glycerol is the most commonly used triol backbone for this material. The chains are randomly polymerized with equal amounts of oxyethylene and oxypropylene groups.

As shown in Table 4.7, the molecular weight of the triols marketed by Dow ranges between 1600 and 4500. They have 50% hydrophile by weight in the chains, and range from an average of 5.1 to 14.6 oxyethylene groups per chain, with oxypropylene groups ranging between 3.9 and 11.1. We assumed an equal distribution in and of chains. Chain end caps and triol sustituents were, in these cases, hydrogen, although that can be varied.

Fig. 4.8 shows the structure of alditol ethoxylated fatty acids. These materials are commonly used in many surfactants, and generally consist of a sugar alcohol backgone to which are attached polyoxyethylene bone to which are attached polyoxyethylene chains and fatty acids, either as esters or can be hydrogen or other groups. Several alditols are used, including sorbitol, mannitol, and other hexitols.

In Table 4.8 the alditols shown range in weight between 3630 and 4010, and contain

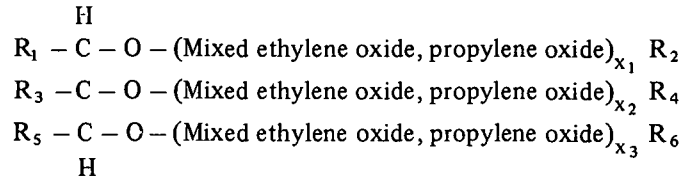

Fig. 4.7. Triol with polyoxyethylene - polyoxypropylene side chains.

Table 4.6. Alkane amine ethoxylates.

Designation	Manufacturer	Approximate molecular wt	Fraction hydrophile	x_1	x_2	R_1	R_2	R_3
MO/15	Armak	487	0.49	2.5	2.5	$C_{18}H_{35}$	H	H

Table 4.7. Triol Chains.

Designation	Manufacuturer	Approximate molecular wt	Fraction hydrophile	x_1	x_2	x_3	R_1	R_2	R_3	R_4	R_5	R_6
112-2	Dow	4500	0.50	14.6[a]	14.6	14.6	H	H	H	H	H	H
15-200	Dow	2600	0.50	8.4	8.4	8.4	H	H	H	H	H	H
3A[b]	Dow	1600	0.50	5.1	5.1	5.1	H	H	H	H	H	H

[a]Mixed chains, x_x is average number of residues assuming equal weight polyoxyethylene, polyoxypropylene.
[b]Not commercially available. Sample was withdrawn from 15-200 during manufacture and polymerization stopped early.

Table 4.8. Alditrol ethoxylated fatty acids

Designation	Manufacturer	Approximate molecular wt.	Fraction hydrophile	x_1	x_2	x_3	x_4	x_5	x_6	R_{odd}	R_{even}
1086	Emery	3630	0.51	6.3[a]	6.3[a]	6.3[a]	6.3[a]	6.3[a]	6.3[a]	H	*b*
1186	Emery	4010	0.54	7.6[a]	7.6[a]	7.6[a]	7.6[a]	7.6[a]	7.6[a]	H	*b*

[a]Assuming equal ethoxylation of branches.
[b]Tall oil acid mixture as follows used for esters: oleic acid 24%, linoleic acid 19%, conjugated linoleic acid 4%, abietic acid 14%, neoabietic acid 7%, related rosin acids 26%, unknown 6%.

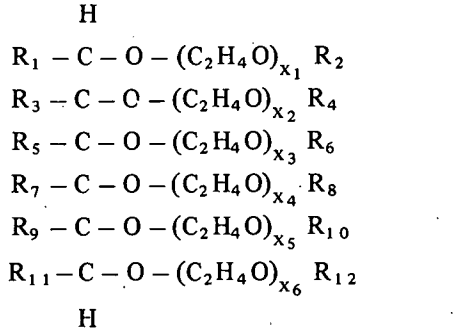

Fig. 4.8. Alditol with ethoxylated fatty acid side chains.

51.0 to 54.5 percent hydrophile. The acids esterified to the polyoxyethylene chains are the tall oil mixture discussed earlier, which includes a fairly broad mixture of saturated and unsaturated fatty acids, and a number of aromatic ring containing chains.

Butoxylated Alkane Esters

Fig. 4.9 shows a butoxylated fatty acids ester. This material is similar to the ethoxylated fatty acids esters shown earlier, and illustrates the polyoxyalkylene range across which such materials are made.

Table 4.9 shows the properties of the material tested, which has a molecular weight of 500 and does not contain a hydrophile by earlier standards. The acid esterified to one end of the 3 unit polyoxybutylene chain is steric acid, and the end cap is hydrogen. As mentioned earlier, end caps vary considerably with manufacturer.

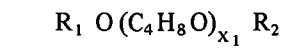

Fig. 4.9. Butoxylated fatty acid ester.

Table 4.9. Butoxylated fatty acid ester.

Designation	Manufacturer	Approximate molecular wt	Fraction hydrophile	x_1	R_1	R_2
BES	Armak	500	0.0	3	$C_{17}H_{35}CO$	H

[a]Mixed chains, x_x is average number of residues assuming equal weight polyoxyethylene, polyoxypropylene.
[b]Not commercially available. Sample was withdrawn from 15-200 during manufacture and polymerization stopped early.

Table 4.10. Ethoxylated mixed groups.

Designation	Manufacturer	Approximate molecular wt	Fraction hydrophile	x_1	R_1	R_2	R_3
CO-530	GAF	484	0.55	6.0	C_9H_{19}	benzene	H

Polyethoxylated Mixed Group Ethers

Fig. 4.10 shows an ethoxylated mixed chain. In this case, the molecule consists of an alkane side chain on an aromatic ring followed by a polyoxyethylene block and an end cap.

The material shown in Table 4.10 is Igepal CO-530, which contains 54.8 percent hydrophile, or 6 repeating groups of polyoxyethylene. The alkane tail of the molecule contains 9 carbons with 19 hydrogens, and the end cap is a hydrogen unit.

$$R_1\ R_2 - O - (C_2\ H_4 O)_{x_1}\ R_3$$

Fig. 4.10. Mixed group ether of polyoxyethylene.

COMMON FEATURES

These materials have in common the presence of at least one polyoxyalkylene chain having a repeating unit containing two to four carbons. They have various chain end caps and structures, and a fairly wide molecular weights and polyoxyalkylene contents. Because these materials are a part of a broad industrially available group of surfactants, there is a substantial amount of patent literature in this general area.

5. *Fualex* Using Pure Hydrocarbons

Fualex uses a combination of a hydrocarbon and a surface active agent to extract alcohols from an aqueous solution, such as a fermentation broth. Appropriate combinations of hydrocarbon and surfactant have to be found. In order to determine useful combinations, the surfactants shown in *Surfactant Structure and Properties*, were tested with hydrocarbons representative of fuels and refinery streams. The hydrocarbons used were heptane, decane, dodecane, and toluene. As discussed in *Materials and Methods*, small shake flask experiments where performed. Hydrocarbon - aqueous ratios ranging from 0.01 to 1 v/v were used, and surfactant concentrations ranging between 0.1 and 1% w/v of the aqueous phase were used. All of the surfactants described in Chapter 4 were tested, although only a fraction of the results will be described. As might be expected, some combinations were markedly better than others. In this and the following chapter, the trends are illustrated. Persons wanting more information on individual systems or groups or systems are encouraged to request it.

Some general observations on the extraction systems are in order. We have observed extraction of alcohols in the presence of hydrocarbons to be increased only when an emulsion is formed. In general, the emulsions which are formed have droplet sizes on the order of 1 to 3 μm, and appear white and pasty. An occasional emulsion appeared bluish and very finely divided. In these cases, the bluish color would often extend into the aqueous. Emulsions could be formed so that the hydrocarbon phase began to become discontinuous, particularly where very small amounts of hydrocarbon were used. By virtue of density, the emulsion became a middle phase.

A few small fermentations using decane and BASF-Wyandotte surfactants have been conducted. In these fermentations, the emulsified phase seems to form during culture growth, and is more readily separated than the phases from shake flask tests, as might be expected. We did not find any apparent diminution of growth rate in the presence of decane; however, mixed organic streams which contain aromatic rings might adversely affect producing cultures. Total alcohols, 5% w/v, used in extractions reflect normal fermentation product concentrations.

HEPTANE

Heptane was the extractant most commonly used, primarily because it is a close analog to gasoline. We investigated the effects of temperature, salt addition to the aqueous, oil - water ratio, and surfactant concentration on alcohols extraction.

Temperature Effect

Table 5.1 compares extractions several surfactants at 20 and 37 C. The hydrocarbon - aqueous ratio used in this case was 1.0, and the surfactant concentration was 0.25% w/v aqueous. With the exception of BASF-Wyandotte 25R2, a *Pluronic R* surfactant, the amount of alcohols extracted increased with increasing temperature. Neutral solvents fermentations can be performed at 50 C and the fact that separations appear better at above ambient temperatures could be advantageous.

Salt Effect

Effect of added 10 m*M* NaCl was mixed, as shown in Table 5.2. The performances of some types of surfactants were slightly improved, while those of others were slightly

Table 5.1. Alcohols extracted using selected surfactants at 0.25% w/v and a hydrocarbon : aqueous ratio of 1.0 at 20 and 37 C.

	Fraction removed, 20 C			*Fraction removed, 37 C*		
Surfactant	Ethanol	Isopropanol	Butanol	Ethanol	Isopropanol	Butanol
BES	0.11	0.02	0.22	0.19	0.14	0.34
25R2	0.30	0.32	0.36	0.11	0.15	0.30
P200DO	0.09	0.01	0.21	0.17	0.10	0.31
P103	0.28	0.29	0.34	0.36	0.42	0.51
31R4	0.34	0.36	0.38	0.28	0.33	0.45
P400DO	0.09	<0.01	0.21	0.17	0.11	0.32
25R5	0.30	0.31	0.35	0.36	0.42	0.51
HA550	0.32	0.33	0.36	0.32	0.36	0.48
17R8	0.36	0.36	0.39	0.32	0.36	0.48
25R8	0.32	0.33	0.36	0.34	0.38	0.50
T1508	0.36	0.36	0.38	0.36	0.40	0.50

Table 5.2. Effect of NaCl on alcohols extracted using selected surfactants at 0.25% w/v and a hydrocarbon : aqueous ratio of 1.0 at 20 C.

	Fraction removed, distilled water			*Fraction removed, 10 mM NaCl*		
Surfactant	Ethanol	Isopropanol	Butanol	Ethanol	Isopropanol	Butanol
P2000	0.11	0.17	0.30	0.09	0.13	0.24
P4000	0.13	0.17	0.30	0.09	0.13	0.27
25R2	0.11	0.15	0.30	0.36	0.31	0.46
P103	0.36	0.42	0.41	0.34	0.36	0.45
31R4	0.28	0.33	0.45	0.36	0.38	0.47
15-200	0.34	0.37	0.47	0.21	0.25	0.35
112-2	0.09	0.14	0.30	0.11	0.14	0.25
25R5	0.36	0.42	0.51	0.34	0.36	0.44
HA550	0.32	0.36	0.48	0.38	0.31	0.50
17R8	0.32	0.36	0.48	0.36	0.38	0.46
25R8	0.34	0.38	0.50	0.38	0.41	0.48
T1508	0.36	0.40	0.50	0.43	0.35	0.49

worsened. The statistical analysis package used, *SAS-79*, indicated that salt concentration over the range investigated had little overall significance as a variable. The smallness of the effect at such low salt concentrations is not surprising in view of the non-ionic nature of the surfactants used

Hydrocarbon to Aqueous Ratio

Table 5.3 shows the effect of hydrocarbon - aqueous ratio on the fraction of total alcohols extracted. In most cases, the fraction extracted is higher at a hydrocarbon - aqueous ratio of 0.01, dips to its lowest point around 0.1, and rises again at larger ratios. This may be the result of a favorable surfactant - hydrocarbon ratio at low hydrocarbon concentrations and to classic

Table 5.3. Fraction of total alcohols extracted using selected surfactants at 0.25% w/v and variable hydrocarbon:aqueous ratios at 20 C.

	Heptane : aqueous ratio				
Surfactant	0.01	0.03	0.05	0.1	1.0
None	0.02	0.01	0.05	0.07	
P2000	0.22	0.14	<0.01	0.07	
P4000	0.23	0.21	0.10	0.09	
L61	0.23	0.25	0.09	0.10	0.32
L62	0.26	0.23	0.11	0.11	0.34
25R2	0.26	0.23	0.07	0.11	0.34
L122	0.25	0.22	0.08	0.11	0.33
P103	0.24	0.22	0.09	0.11	0.32
31R4	0.26	0.23	0.06	0.12	0.37
15-200	0.23	0.22	0.09	0.18	
112-2	0.22	0.22	0.09	0.10	
25R5	0.14	0.22		0.11	0.34
HA550	0.16	0.22	<0.01	0.12	0.35
17R8	0.25	0.22	0.08	0.24	0.38
25R8	0.22	0.22	0.07	0.12	0.35
T1508	0.28	0.23	0.09	0.12	0.38
E200	0.13	0.21	<0.01	0.02	0.28
E400	0.12	0.13	<0.01	0.04	0.28
E600	0.14	0.13	<0.01	0.04	0.28
E1000	0.13	0.12	<0.01	0.04	0.26
E1450	0.13	0.13	<0.01	0.05	0.28
E4000	0.18	0.18	<0.01	0.05	0.30
E8000	0.21	0.21	0.01	0.08	0.35

Table 5.4. Fraction of total alcohols extracted using selected surfactants at 0.25% w/v and hydrocarbon:aqueous ratio of 0.1 at 20 C.

	Fraction removed		
Surfactant	Decane	Dodecane	Toluene
AM121	0.04	0.01	0.13
GO20	0.08	0.04	0.22
M18	0.10	0.10	0.08
0A	0.05		0.08
OA-10	0.03	0.02	0.06
P100S	0.06	0.02	0.09
SDD052	0.05		0.12
TW80	0.02	0.02	0.15
TX100	0.09		0.14
0/20	0.06	0.04	0.07
2646	0.08	0.03	0.11
HA550	0.11	0.08	
792	0.09	0.02	0.09
CO-530	0.10	0.06	0.09
P4000	0.10	0.10	0.05
L62	0.09	0.10	0.05
L122	0.12	0.07	0.01
P103	0.12	0.08	0.01
E4000	0.04	0.01	0.09
E8000	0.07	0.07	0.11
31R2	0.11	0.09	0.07
31R4	0.13	0.07	0.01
17R8	0.12	0.06	0.01
25R8		0.07	0.23
T1508	0.13	0.08	0.20
60/20	<0.01	0.02	0.13
RE22	0.08	0.04	0.08
242/25	0.01	0.03	0.15
RE20	<0.01	0.07	0.10
15-200	<0.01	0.12	0.24
112-2	0.06	0.10	
1186	<0.01		0.07
BES			0.05

extraction of alcohols into the hydrocarbon at higher hydrocarbon to aqueous ratios.

Surfactant Concentration

Statistical analysis indicates that the data do not show a significant effect of surfactant concentration in the range of 0.1 to 1.0 % w/v as a group. Individual surfactants do occasionally show such an effect, but it appears minor compared to the effect of hydrocarbon - aqueous ratio.

OTHER HYDROCARBONS

Table 5.4 shows the fraction of total alcohol extracted by selected surfactants at a hydrocarbon to aqueous ratio of 0.1 and 20 C using decane, dodecane, and toluene. Toluene is generally the most effective hydrocarbon, followed by decane and dodecane. Decane and dodecane are less effective than is heptane, although toluene is often somewhat more effective than is heptane.

CONCLUSIONS

It appears possible to remove roughly 1/4 of the total alcohols by extracting an aqueous alcohols system with a combination of 0.25% w/v of several common surfactants and 0.01 heptane extraction ratio. The alcohols are removed as part of an emulsion formed between and of the hydrocarbon and aqueous phases.

6. *Fualex* Using Mixed Hydrocarbons

We were able to obtain some unadulterated gasoline, premier diesel fuel, and furance oil from Amoco through the kindness of Dr. H. R. Froning and his staff. His staff indicated that such streams could be made available on a commercial basis to interested parties, although Amoco would probably prefer to use some conventional additives, such as antioxidants, prior to shipment. We expected that these materials, because they contained more branched chains and aromatic groups than did heptane, decane, and dodecane, would be more effective extractants. As earlier, we used aqueous solutions which contained approximately 5% w/v total alcohols.

GASOLINE

A comparison of gasoline and heptane at an oil-water ratio of 0.1, 20 C, and no added NaCl is shown in Table 6.1. Although it should be noted that this is the least favorable oil-water ratio, the gasoline can remove up to 14 or 15% of the input solvents. On the average, it is better than heptane.

Table 6.1. Fraction of alcohols extracted using selected surfactants at 0.25% w/v and a hydrocarbon : aqueous ratio of 0.1 at 20 C.

	Heptane			*Gasoline*		
Surfactant	Ethanol	Isopropanol	Butanol	Ethanol	Isopropanol	Butanol
P4000	0.08	0.06	0.10	0.08	0.09	0.11
L61	0.07	0.10	0.10	0.13	0.14	0.15
L62	0.07	0.06	0.13	0.08	0.14	0.12
L122	0.0.7	0.04	0.13	0.04	0.11	0.13
25R2	0.08	0.0.6	0.13	0.17	0.15	0.14
31R2	0.07	0.2	0.10	0.08	0.10	0.13
P103	0.06	0.05	0.13	0.04	0.10	0.14
31R4	0.08	0.05	0.14	0.13	0.12	0.15
25R5	0.08	0.06	0.14	0.13	0.14	0.15
HA550	0.08	0.10	0.14	0.08	0.13	0.13
15-200	0.19	0.18	0.18	0.13	0.13	0.16
112-2	0.08	0.09	0.11	<0.01	0.04	0.07
17R8	0.21	0.21	0.24	0.13	0.11	0.13
25R8	0.08	0.06	0.14	0.13	0.14	0.14
T1508	0.08	0.06	0.14	0.13	0.14	0.14
E400	0.03	0.01	0.05	0.04	0.01	<0.01
E1000	0.03	0.01	0.04	0.04	0.1	0.02
E4000	0.04	0.04	0.06	0.08	0.13	0.16
E8000	0.09	0.06	0.09	0.17	0.14	0.13

PREMIER DIESEL

As expected, the premier diesel fuel was more successful as an extractant than was decane. A comparison between these at an oil-water ratio of 0.1, 20 C, and no added salt is shown in Table 6.2. Diesel fuel was the most successful extractant which we used at this temperature and oil-water ratio, with fractions as high as 0.2 of the alcohols extracted. On the average, it did about twice as well as did decane, and the results were more consistent in a given surfactant type. It is particularly interesting to note the difference between the amounts of alcohols extracted.

FURNACE OIL

Furnace oil did somewhat better than did dodecane, but not as well as did premier diesel fuel. In both cases, the surfactants which contained polyoxyethylene alone were poor performers. However, both block and random polyoxyethylene - polyoxypropylene surfactants and derivatives of polyoxyethylene and alkane or alkene acids gave good relative performance, as shown in Table 6.3. With furnace oil, it is possible to obtain a mixture which extracts about 0.15 of the alcohols contained in the aqueous.

CONCLUSIONS

It appears that mixed hydrocarbons or hydrocarbons included in the mixtures used are somewhat more effective than the corresponding pure straight chain hydrocarbons of the same carbon number. It appears that these materials may makc suitable extractants for alcohols from neutral solvents fermentation broths in conjuction with matched surfactants after fermentation and perhaps during fermentation if potential microbial toxicity problems can be overcome.

Table 6.2. Fraction of alcohols extracted using selected surfactants at 0.25% w/v and a hydrocarbon : aqueous ratio of 0.1 at 20 C.

	Decane			*Premier diesel*		
Surfactant	Ethanol	Isopropanol	Butanol	Ethanol	Isopropanol	Butanol
P4000	0.08	0.08	0.10	0.19	0.16	0.20
L61	<0.01	0.01	<0.01	0.15	0.16	0.21
L62	0.05	0.05	0.10	0.19	0.15	0.20
L122	0.10	0.09	0.13	0.19	0.14	0.20
25R2	0.10	0.10	0.14	0.19	0.15	0.15
31R2	0.08	0.09	0.12	0.19	0.15	0.15
P103	0.08	0.09	0.13	0.19	0.15	0.20
31R4	0.10	0.10	0.14	0.19	0.14	0.20
25R5	0.10	0.10	0.13	0.15	0.17	0.19
HA550	0.10	0.09	0.12	0.15	0.17	0.18
112-2	0.05	0.05	0.07	0.15	0.15	0.20
17R8	0.10	0.10	0.12	0.22	0.17	0.18
25R8	0.08	0.06	0.02	0.22	0.17	0.18
T1508	0.10	0.10	0.14	0.22	0.18	0.20
E4000	0.03	0.03	0.04	0.15	0.14	0.16
E8000	0.05	0.07	0.08	0.15	0.15	0.18

Table 6.3. Fraction of alcohols extracted using selected surfactants at 0.25% w/v and a hydrocarbon : aqueous ratio of 0.1 at 20 C.

	Dodecane			*Furnace oil*		
Surfactant	Ethanol	Isopropanol	Butanol	Ethanol	Isopropanol	Butanol
P4000	0.05	0.08	0.12	0.16	0.12	0.16
L61	0.05	0.06	0.10	0.12	0.12	0.16
L62	0.05	0.08	0.11	0.16	0.13	0.16
L122	0.05	0.06	0.07	0.12	0.13	0.15
25R2	0.08	0.08	0.10	0.16	0.14	0.18
31R2	0.08	0.07	0.09	0.16	0.14	0.16
P103	0.08	0.07	0.08	0.16	0.13	0.13
31R4	0.08	0.06	0.07	0.16	0.09	0.08
25R5	0.05	0.06	0.07	0.16	0.13	0.14
15-200	0.10	0.10	0.13	0.12	0.13	0.16
112-2	0.05	0.07	0.11	0.16	0.12	0.16
17R8	0.05	0.05	0.06	0.12	0.14	0.13
25R8	0.08	0.07	0.07	0.08	0.06	0.04
T1508	0.08	0.08	0.08	0.08	0.12	0.14
E4000	<0.01	<0.01	0.02	0.08	0.10	0.07
E8000	0.03	0.04	0.08	0.08	0.10	0.12

7. Practical Implications

It is often difficult to predict the form that a new technological development will ultimately take. However, since the *Fualex* process touches on a number of current developments, we will try to delineate the effect that it might have if it were widely used. We expect that the bench scale work will translate in actual operation with a minimum of engineering difficulty.

PRODUCTION

A fermentation facility using *Fualex* would probably be similar in appearance and operation to one which employed classical solvent extraction for neutral solvents removal. The hydrocarbon and surfactant used probably would be introduced into a fermentation vessel at either the stirrer or through nozzles at the bottom of the vessel. Retrofitting to existing fermentation equipment, which is basically closed agitated tanks, is not anticipated to pose an engineering problem. The emulsion formed could collect at the top of the broth and be removed for further use. Depending on the use desired, the composition of the emulsion could be modified, or it might be broken and the components separated. The former might be expected with diesel fuel, and the latter, in gasoline.

REGULATORY

There are current regulatory and other institutional advantages and disadvantages to neutral solvents and ethanol use. A major advantage of neutral solvents use as opposed to ethanol use is relative freedom from regulation under Alcohol, Tobacco, and Firearms legislation since neutral solvents are not potentially potable. This can permit use of more efficient and more adjustable plant design and operation, since, for example, unsealed rather than sealed, fittings, can be used, and since less federal information on plant operations is required.

There is a similar advantage to using neutral solvents in diesel fuels. The composition of diesel fuel appears at the present time not subject to the Clean Air Act, although the Act covers the composition of gasolines. Although this could be changed by further regulation, it would mean that currently the waiver and test procedure under the Clean Air Act, with the several month waiting periods, would not have to be followed for diesel fuel.

Disadvantages include the need to clarify the tax exemption status of neutral solvents, since, at the time of legislation, ethanol and methanol were considered the major commodities for this use. However, the legislation does cover biomass derived alcohols, so it is not unreasonable to expect coverage by the legislation. This is also true in many state laws, where alcohol may be interpreted to mean ethanol. This is more important than it may appear in that tax exemptions amount to a credit of $1.00 or more per gal of alcohols, which is roughly equal to the cost of input grain for alcohols production.

INTERFACES

Fualex touches on many other ongoing or developing technologies. For example, understanding of the formation of emulsified fuels may help in the development of fuel blends which can tolerate enough water to decrease the need for ethanol dewatering. In turn, incorporation of small amounts of water and neutral solvents in fuels should, according to available literature, have a major effect on automotive and stationary

power generation emissions, which could contribute to U.S. energy sufficiency without the sacrifice of environmental concerns.

The intention of the U.S. Army to field a fire resistant diesel fuel by the mid-1980's will cause more attention to be directed to this area, and should increase the acceptability of water-containing fuels (Wetherford, et al 1979). We are unsure of the effect that safety improvements possible with these fuels will have, or whether they extend to cover fuels containing neutral solvents. Transportation safety concerns may affect regulation and insurance rates.

From Wetherford, *et al*, it appears that some materials testing and development will be required. Urethane polymers, in particular, were adversely affected by fire resistant fuels emulsions.

Another consideration is the reduced energy costs inherent in neutral solvents distillation, due to the presence of a miscibility gap between butanol and water and to higher component volatility.

8. Materials and Methods

The tests which have been performed to date have been bench tests. In general, we analyze standards cocurrently with samples, and standards are carried through all of the steps of sample handling. The gas chromatograph is restandardized every fifth sample, and the recalibration procedures use a triple injection in a weighted average. The data was analyzed using the *Statistical Analysis System - 79*, which is a resident computer statistics program. Standards are reproducible to about 3% of the content of each alcohol and results were calculated based on removal from the aqueous.

SHAKE FLASK TESTS

Bench tests to evaluate the extraction of *n*-butyl, *i*-propyl, and ethyl alcohols from aqueous solutions in the presence of an organic layer were performed. In each case 10 ml of an aqueous solution containing 5% total alcohols in a ratio of 7:3:1 butanol:isopropanol: ethanol was contacted with a predominantly with a hydrocarbon solution in a 50 ml glass stoppered flask. Several glass beads between 2 mm and 6 mm in diameter were added to encourage mixing and the flasks were shaken for a period of at least 2 hr. After shaking, the flasks were thoroughly emulsified by either agitation with a Vortex *Genie* model K-550-G mixer on a setting of 10 or by being pushed in and out of a Comstock 10 ml syringe pipetter with a 4 in. No 14 cannula. Eight ml were withdrawn from each flask and placed in a 13 × 100 mm test tube. The tubes were centrifuged at 7,000 rpm in a Sorvall GSA rotor. During centrifugation, temperature was maintained constant with the incubation temperature. Alternatively, 5 ml samples were similarly withdrawn, placed in 12 × 75 mm test tubes, and centrifuged at 5,000 rpm in a swinging bucket rotor.

After centrifugation, the aqueous layer was removed and placed in a sample vial and anaylzed using a Varian 1520B gas chromatograph equipped with a CDS 111 data and control system and a model 8000 autosampler. The alcohols in the samples were separated using a 1/8 in X 10 ft Porapak P column at 160 C. Alternatively, a Varian 3700 gas chromatograph equipped with a CDS 111 data and control system and a model 8000 autosampler was used. The column used with this system was the same, but a linear +10 C/min temperature program was used with this instrument. Because aqueous samples were analyzed to determine alcohol reduction, controls containing alcohols in water were run cocurrently, as were hydrocarbon controls.

We have reported the data in terms of alcohol fraction extracted, rather than using a distribution coefficent, because of the changes in phase number, density, and volume.

REAGENTS

Surfactants. The grades used were commercial grades supplied as standard samples by manufacturers. These materials are mixtures of surfactants having average chain lengths. Manufacturers' literature claimed a molecular weight distribution of about ± 10% of polyoxyalkylene weight in most cases. We are particularly grateful for the special efforts of Dr. Niu of BASF-Wyandotte and Dr. Trapp of DOW, who found us samples which were particularly interesting chemically.

Chemicals. Analytical reagent grades were generally used. The *n*-heptane was analytical reagent grade supplied by Mallincrodt, as were the *i*-propanol and toluene. The *n*-butanol, decane, and acetone were Fisher certified reagents. The dodecane was MCB practical grade, 95% pure. Ethanol was Publicker USP 200 proof.

Petroleum distillates. We obtained refinery run samples without additives through the courtesy of Dr. H. R. Froning of Amoco research and his staff.

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