



PROJECT REPORT No. OS25

**POTENTIAL APLICATIONS
OF PRODUCTS FROM OILSEED
RAPE IN THE OFFSHORE OIL
AND GAS INDUSTRY**

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**POTENTIAL APPLICATIONS OF PRODUCTS FROM
OILSEED RAPE IN THE OFFSHORE OIL
AND GAS INDUSTRY**

by

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SUMMARY

During the exploration and production of oil and gas, a vast quantity of chemicals are consumed. Oil industry operations can be divided into two categories, drilling and production, and it has been estimated that these activities offer a combined annual market of over two-hundred thousand tonnes of process chemicals. Further, it is interesting to note that of these two-hundred thousand tonnes, over one-hundred thousand tonnes are 'lost' into the environment each year. As a consequence, there are strong regulatory pressures on the oil and gas companies to move towards the use of 'greener' chemicals.

Oilseed rape is a source of a variety of products, the most important of which are:

- (i) rapeseed oil;
- (ii) fatty acids;
- (iii) glycerides;
- (iv) glycerol; and
- (v) meal.

These products exhibit a range of physico-chemical properties which are of interest to the oil and gas industry, and could, for example, find use in applications such as: base oils and lubricity aids for both oil based and water based drilling fluids; surfactants for use in demulsifiers, emulsion breakers and oil-wetting agents; shale stabilisers for use during drilling; and absorbents for treating oil or chemicals spills on a drilling or production platform.

In short, therefore, the offshore oil and gas industry represents a large and on going market for chemicals many of which could, potentially, be formulated using materials derived from oilseed rape.

This specific investigation was predominantly a practical study during which the most promising new products were subjected to a laboratory evaluation to assess their performance under controlled conditions.

Five new oilseed rape based products were developed and assessed, these being:

- (i) a drilling mud emulsifier;
- (ii) an oil spill emulsion breaker;
- (iii) a combined gas drying agent and anti-freeze;
- (iv) a corrosion inhibitor; and
- (v) a general purpose absorbent.

The initial tests indicated that these products performed as effectively as traditional products.

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1 AIMS AND OBJECTIVES

The aim of this project was to identify new potential areas of application for products derived from oilseed rape to the offshore oil and gas industry. The investigation was a predominantly practical study, during which the most promising new materials were subjected to a laboratory evaluation to assess their performance under controlled conditions.

Oilseed rape comprises a broad range of material types and molecular species, eg triglyceride oil, meal and straw. The triglyceride oil can be further broken down, either completely, to yield free fatty acid (of which these are several distinct types) and glycerol, or partially, to give fatty acids and mono- and di-glycerides. The fatty acids can be modified by chemical reaction to give a range of other functional groups, eg esters, alcohols, amines and amides. Oilseed rape, therefore, has the potential to be a source of a very broad range of chemical end-products and intermediates exhibiting an equally broad range of chemical properties, and hence should find usage in a number of offshore oilfield activities.

2 INTRODUCTION

Chemicals are used in a wide range of applications by the offshore oil and gas industry. Offshore operations are generally divided into two activities, drilling and production, and similarly, chemicals are often described as being either drilling chemicals or production chemicals.

2.1 DRILLING CHEMICALS

Drilling an oil well requires the use of a drilling fluid or mud. The fluid serves a number of functions, including:

- (i) transportation of the cuttings to the surface;
- (ii) balancing of downhole pressures; and
- (iii) lubrication of the drill bit.

The muds can be either water based or oil based, and contain a variety of chemical additives, eg weighting agents, viscosifiers, clay stabilisers, emulsifiers and fluid-loss additives.

The quantity of chemicals consumed each year by North Sea operations varies with the extent of exploration that takes place, but is of the order of one hundred thousand to four hundred thousand tonnes^[1]. The need for environmentally responsive materials is highlighted when one considers that approximately 60% of these chemicals are 'lost' into the environment each year^[2].

The different chemical types and estimate of the quantities consumed by North Sea drilling operations are shown in Table 1.

TABLE 1 Drilling Chemicals/Annual Usage

DRILLING CHEMICAL	ANNUAL CONSUMPTION (tonnes/year)
Weight Agents	360,000
Lost Circulation Chemicals	3,400
Lignosulphonates	2,800
Polymers	8,400
Asphalts	1,800
Defoamers	260
Biocides	117
Corrosion Inhibitors	212
Scale Inhibitors	536
Lubricants	247
Stuck-Pipe Release Agents	131
Dispersants	559
Oxygen Scavengers	42
Surfactants	4,100
Cutting Cleaners	57
Shale Inhibitors	3,300
Emulsifiers	19
Other	1,200

2.2 PRODUCTION CHEMICALS

Once an oil well has been successfully drilled the flow of reservoir fluids can only be maintained by constantly dosing the system with chemicals^[3]. The main chemical types utilised, with a brief description of their function, are listed below.

DEMULSIFIERS

Oil is normally produced together with dissolved or free gas and water (formation water). The water content of the oil can vary from less than 0.5% to over 90% and normally increases during the lifetime of the well. When a large proportion of water is present, some will be in the form of 'free' water which readily separates from the oil. Some water, however, will also be present in an

emulsified form, the emulsion being stabilised by naturally occurring surfactants in the oil^[4]. The emulsified water is removed by the addition of demulsifiers which destabilise the emulsion and allow the water droplets to coalesce and separate. Demulsifiers are generally a blend of surfactants in a carrier solvent and can be either anionic, cationic, non-ionic or amphoteric in nature.

DE-OILING CHEMICALS

The water droplets which separate from the oil often contain finely dispersed oil droplets. It is necessary to reduce the amount of oil in the water before disposal and this is achieved by de-oiling chemicals. De-oiling chemicals are generally highly charged polymeric species, *eg* polyamines, which function by neutralising the charge on the dispersed oil droplets thus promoting their coalescence and separation.

CORROSION INHIBITORS

The oil production equipment is subject to corrosion from the brine associated with the oil and also acidic gases such as carbon dioxide or hydrogen sulphide. Corrosion inhibitors are added into the fluid streams to minimise corrosion and generally function by forming a thin, protective film over metal surfaces. They can be produced from a very broad range of chemical functionalities but are often formulated from amines and amides.

SCALE INHIBITORS

Scale deposition inside flowlines and equipment occurs most commonly when the formation water becomes super saturated with the carbonates or sulphates of barium, calcium or strontium. Alternatively, scale can be formed when seawater is injected into the reservoir, for example during secondary oil recovery. Sea water is generally rich in sulphate ions and this precipitates with the barium, calcium and strontium ions present in the formation water. Typical chemicals used to inhibit scale formation are organic phosphates, phosphonates and polyacrylates. These are injected into the reservoir fluids and operate by inhibiting inorganic crystal nucleation and growth.

WAX INHIBITORS

Many crude oils exhibit crystallisation of aliphatic long chain hydrocarbons (waxes) as the temperature decreases from the reservoir, through the flowlines, to the stock tank. As the waxes crystallise, reduction in flow and eventual plugging of pipelines and facilities can occur. As an alternative to the addition of wax solvents or mechanical means, wax crystals can be restricted by adding wax inhibitors to the system. These are often polymeric in nature, *eg* polymethyl methacrylates, and function by co-precipitating with the wax crystals thus disrupting the wax lattice and preventing crystal growth.

GAS DRYING

To reduce corrosion of gas pipelines and to suppress hydrate formation, *ie* the formation of ice crystals around gas molecules, gas is dried by passing it through a counter current column with glycol. The glycol is normally recovered by boiling off the water.

2.2.1 PRODUCTION CHEMICAL CONSUMPTION

The total quantity of production chemicals used offshore is considerably less than that of drilling chemicals, but is of the order of twenty thousand tonnes per year, with approximately 25% of these being discharged into the environment^[5].

Production chemical types and an estimate of the quantities used are given in Table 2.

Other oilfield activities which consume large quantities of chemicals include cementing operations, where of the order of ninety thousand tonnes of chemicals are used annually (over eighty thousand tonnes of this is cement itself), and also in the stimulation of the oil reservoir. This involves the use of brines and acids to clean the borehole and to fracture the oil bearing formations (giving higher permeabilities), and consumes approximately thirty thousand tonnes of chemicals each year^[6].

Therefore, in total, the North Sea for market for chemicals is huge and although varying from year to year, can be of the order of five hundred thousand tonnes per annum.

TABLE 2 Production Chemicals/Annual Usage

PRODUCTION CHEMICAL	ANNUAL CONSUMPTION (tonnes/year)
Demulsifiers	400
De-Oilers	200
Corrosion Inhibitors	2,400
Scale Inhibitors	1,700
Biocides	2,500
Oxygen Scavengers	1,200
Antifoam Agents	140
Flocculants	200
Surfactants	24
Detergents	92
Gas Treatment	9,300
Wax Inhibitors	200
Other	1,200

2.3 RAPESEED OIL AS A RAW MATERIAL FOR OFFSHORE CHEMICALS

Rapeseed oil per se, ie the triglyceride oil, is a high flashpoint (>300°C), high lubricity material that is currently used as a minor component of water based drilling muds^[7]. Transesterified rapeseed oil, eg 2-ethylhexyl oleate, has been used as a base oil in so-called synthetic mud systems (SMS)^[8]. These synthetic oils are generally more expensive than the traditional oils used in oil

based drilling muds and, more recently, the potential for using rapeseed oil itself as a drilling mud base oil has been extensively evaluated^[9].

Rapeseed oil can be readily hydrolysed to its constituent fatty acids and glycerol. Fatty acids are chemically reactive species which can be easily converted into a wide range of chemical intermediates or end-products. Examples include soaps (sodium and calcium), fatty alcohols, esters, amines, amides, sulphates and sulphonates. All of these chemical functionalities are found in the broad spectrum of offshore chemicals and hence, in theory, rapeseed oil should have a very broad range of application.

In the past, price has been a key element in selecting chemical raw materials and, because of this, fatty acids derived from tall oil, a by-product of the wood pulp industry, have been the preferred choice. Cost will undoubtedly remain a key issue when selecting oleochemical raw materials and, at present, this does put rapeseed oil at a disadvantage compared to less expensive oils. A possible solution for this would be to use crude rapeseed oil as the feed-stock but care would have to be taken to ensure that the non-glyceride components of the oil, *ie* the gums, did not interfere with the performance of the finished product. An alternative approach would be to concentrate on developing very high performance, or even multifunctional products, where the comparative cost between tall oil derived and rapeseed oil derived materials would be of lesser significance.

The glycerol derived from the hydrolysis of rapeseed oil has similar chemical properties to the glycols used offshore, *ie* mono-ethylene and tri-ethylene. Glycerol is more expensive than both of these glycols, *ie ca* £700/tonne for the glycols against £1,100/tonne for glycerol, but could offer both a better technical performance and improved health and safety than the glycols. A very large quantity of glycols and other alcohols are discharged into the seas each year. Although these are not under current testing regimes seen as being ecologically damaging^[10], environmental impact on any scale must be considered, and glycerol may also offer certain advantages in this area.

3 APPLICATIONS, EXPERIMENTAL PROCEDURES AND RESULTS

3.1 CHEMICALLY MODIFIED RAPESEED OIL

3.1.1 Drilling Mud Emulsifier

Oil based drilling muds comprise emulsions of oil and water. They are generally dispersions of water throughout a continuous oil phase, *ie* they are invert or water-in-oil emulsions, and are stabilised by the addition of surfactants.

In this study a surfactant was prepared from rapeseed oil derived fatty acids by reacting them with two equivalents of diethanolamine to give the relevant fatty acid diethanolamide. A standard literature procedure^[11] was used to prepare the diethanolamide and is summarised here.

Diethanolamine (29.2 g) was placed into a beaker (100 ml) along with rapeseed oil derived fatty acids (40 g). The mixture was stirred at room temperature, and gave a pale yellow, very viscous paste which was the diethanolammonium salt of the fatty acids. The stirred paste was heated over a small Bunsen flame until it reached a temperature of 180°C, and, by repeatedly removing and replacing the Bunsen, the mixture was maintained at this temperature for *ca* 20 minutes. On

cooling the product became a viscous, deep orange coloured liquid. Infrared analysis (KBr disc) of the product indicated a strong absorption at $3,300\text{ cm}^{-1}$ and also at $1,615\text{ cm}^{-1}$ both of which are characteristic of amides.

The product was then used with no further purification as an emulsifier in an oil-based drilling mud. The composition of the mud is shown in Table 3.

TABLE 3 Drilling Mud Composition

DRILLING CHEMICAL	QUANTITY (g)
Base Oil*	150
Emulsifier	10
Organophilic clay	10
Brine†	150
Barite	100

* The base oil was Ultidrill, a synthetic hydrocarbon

† The brine comprised calcium chloride solution (20%w/w)

Oil-based drilling muds are emulsions, *ie* they comprise an immiscible oil and aqueous phase 'held-together' by an emulsifier. The mud's emulsion stability, and hence the emulsifying power of the emulsifier, is determined by measuring its breakdown voltage. Several emulsion stability meters are available and, in this instance, the device manufactured by OFI, Model ESM-30A, was employed.

The mud was formulated with the diethanolamide emulsifier, and aged at 120°C for sixteen hours to simulate the downhole temperatures that the mud would be subjected to in the 'field'. The emulsion stability of the mud was then determined. A replicate mud was also prepared but a commercially available drilling mud emulsifier (based on imidazoline chemistry) was used in place of the rapeseed oil derived product. The results obtained are shown below in Table 4.

TABLE 4 Drilling Mud Stabilities

EMULSIFIER	BREAKDOWN VOLTAGE (volts)
Rapeseed Oil Based	264
Commercial	104

The results obtained clearly showed that rapeseed oil derived fatty acids could be used to prepare an effective drilling mud emulsifier which performed better than a commercially available products.

3.1.2 Oil Spill Emulsion Breaker

When oil is spilled at sea it is immediately subject to a range of processes, for example evaporation, solubilisation and emulsification, that greatly change its composition and physical properties. These processes are collectively described as weathering, and can result in an oil being converted from a low viscosity fluid into a high viscosity water-in-oil emulsion which is resistant to both natural dispersion processes and also chemical dispersants. When this situation is encountered, the emulsions can be physically removed from the water surface and treated with emulsion breakers to 'split' the retrieved emulsion back into oil and water and so recover the oil.

Oil spill emulsion breakers are generally blends of surfactants, which are usually petroleum based, eg ethylene oxide or octyl sulphosuccinates.

IOE personnel have considerable experience of oil spill emulsion breakers^[12], and in this study a comparison of a rapeseed oil-based product was compared to a highly effective, commercially available product, Inipol IPC.

The rapeseed oil based material was the reaction product of rapeseed fatty acids and a mixture of monoethanolamine and diethanolamine (50/50 mixture) and was prepared in a similar manner to the drilling mud emulsifier described previously. Three emulsion substrates covering the viscosity range 13,000 cP - 27,300 cP were studied. The actual viscosity of an emulsified oil subsequent to an oil spill is dependent on a number of factors. Oil composition, sea temperature and weather conditions (wind speed) all contribute to the viscosity of the emulsion. The emulsions used in this study were, by comparison to literature data^[13], of relatively high viscosity but were realistic. The use of these high viscosity substrates did, however, provide a rigorous test for the prepared emulsion breaker.

The water contents of the three emulsions (volume by weight) were 41% v/w, 65% v/w and 59% v/w and the effectiveness of the emulsion breakers was determined by measuring the volume of water released from the emulsions over a given time period.

The emulsion breaker concentration was 1% v/w of test emulsion, and the test temperature was 8°C. The emulsion (20 g) was placed into a conical flask (100 ml) and the emulsion breaker added. The flask was swirled on an orbital shaker for a total time of 4 hours after which the 'released' water was decanted off and measured. The results obtained are shown in Table 5.

TABLE 5 Comparison of Rapeseed Oil Based Emulsion Breaker with Commercially Available Product

EMULSION BEAKER	EMULSION VISCOSITY(cP)	% EMULSION BROKEN
Rapeseed Oil Based	13,000	50
Inipol IPC	13,000	85
Rapeseed Oil Based	19,000	86
Inipol IPC	19,000	70
Rapeseed Oil Based	27,300	42
Inipol IPC	27,300	46

The rapeseed oil derived product was less effective against the low viscosity emulsion compared with Inipol IPC, more effective against the "medium viscosity" emulsion and comparable against the higher viscosity substrate.

Inipol IPC is an extremely effective product and hence the data produced for the rapeseed oil based sample indicates that it does have considerable demulsifying power.

3.1.3 Rapeseed Oil Derived Corrosion Inhibitors

Corrosion inhibitors used by the offshore industry often comprise nitrogen containing molecules such as amines, amides and quaternary ammonium salts. Rapeseed oil derived fatty acids can be easily converted into these chemical functionalities and, hence, during this evaluation the corrosion inhibition properties of fatty acid based amides and amines were studied.

Fatty acid amides were prepared by reacting oleoyl chloride with one equivalent of amine.

The fatty acid amine used, *ie* oleoylamine, was purchased from Sigma-Aldrich Ltd.

Corrosion prevention properties of the reagents were assessed using a method described in IP135. Briefly, this involved dissolving the test chemical in mineral oil (300 ml, Clairsol 430) adding distilled water (30 ml) and a clean iron nail. The mixture was placed into a stainless steel cell and rotated for 24 hours at 60°C. The degree of corrosion on the iron nail was then assessed. The prepared reagents were dissolved at 0.5% w/v, 0.1% w/v and 0.05% w/v of oil, and are typical additive concentrations for this test method.

3.1.4 Rapeseed Oil Fatty Acid Amides

Three fatty acid amides, *ie* oleic diethanolamide, oleic diethylamide and oleic hexylamide were prepared by reacting equimolar quantities of oleoyl chloride (which can be derived from rapeseed oil) and the relevant amine, *ie* diethanolamine, diethylamine and hexylamine.

The results obtained are given in Table 6.

TABLE 6 Corrosion Inhibition Properties of Rapeseed Oil Derived Amides

REAGENT	CONCENTRATION W/V		
	0.5%	0.1%	0.05%
Oleic diethanolamide	SC	SC	SC
Oleic diethylamide	SC	SC	SC
Oleic hexylamide	SC	SC	SC

SC - SEVERE CORROSION

No corrosion inhibition was found with any of the three amines at any concentration.

3.1.5 Rapeseed Oil Derived Amido-Amines

In this instance oleoyl chloride was reacted with half an equivalent of diaminohexane. The resultant molecule, therefore, contained both an amide group, from reaction between one of the amine functions and the acid chloride, and also an amine group remaining from the original diamine.

The amido-amine product was added to the corrosion cells at the standard dilutions, *ie* 0.1%, 0.5% and 0.01% w/v, and its corrosion inhibition properties assessed.

The results obtained are shown below in Table 7.

TABLE 7 Amido-Amine Corrosion Inhibition Properties

AMIDO-AMINE CONCENTRATION	EXTENT OF CORROSION
0.5%	SC
0.1%	NC
0.05%	SC

SC -SEVERE CORROSION

NC - NO CORROSION

Although severe corrosion was observed at concentrations of 0.5% and 0.01% w/v of the added amido-amine, no corrosion was found at 0.1% w/v concentration.

Several repeats and controls were then carried out at this concentration, and this corrosion inhibition property was confirmed.

This amido-amine did, therefore, appear to exhibit corrosion inhibition properties, but its effectiveness was very concentration dependent.

3.1.6 Rapeseed Oil Derived Amine

Oleylamine (C₁₈H₃₄NH₂) is a fatty amine which can be produced from rapeseed oil fatty acids, *eg* by reduction to a fatty alcohol followed by reaction with ammonia.

In this instance the amine was purchased from Sigma-Aldrich Ltd, Dorset.

The amine was added to the corrosion cells at 0.5%, 0.1% and 0.05% w/v and the normal procedure followed.

The results obtained are given in Table 8.

TABLE 8 Fatty Amine Corrosion Inhibition Properties

SUBSTRATE CONCENTRATION (w/v)	CORROSION EFFECT
0.5%	SC
0.1%	MC
0.05%	NC

SC -SEVERE CORROSION

MC - MODERATE CORROSION

NC - NO CORROSION

Corrosion was observed at the two higher amine concentrations, but at 0.05% w/v of added substrate no corrosion was detected.

A series of repeats and controls at 0.05% w/v oleylamine confirmed this finding.

As with the amido-amine compound described in Section 3.1.5, the fatty amine was able to inhibit corrosion but the effect was concentration dependent.

3.2 GLYCEROL

3.2.1 Glycerol as a Gas Drying Agent

During the production of oil and gas, a significant proportion of water is also produced. This water is obviously of no commercial value and is therefore removed from the oil and gas before it is transported ashore by tanker or pipeline.

The removal of water from oil is achieved using a variety of physical methods *eg* centrifugation, electrostatic coalescers or chemical methods.

Gas drying is achieved by passing the gas through a column containing glycols. The glycol is highly hygroscopic, and absorbs the water from the gas.

However, the process is not 100% efficient and gas hydrates, *ie* gas molecules surrounded by ice crystals, can form in the gas pipeline as it is brought ashore. These hydrates can block the line if they are not treated, and methanol is regularly pumped into the line to inhibit their formation.

In this study, the potential for using glycerol (derived from rapeseed oil) as a gas drying agent was investigated.

Unfortunately, due to health and safety restrictions, a wet gas stream could not be produced in the laboratory. The process was simulated, however, using a light mineral oil which had been saturated with water. Although not ideal, this gave an indication of the ability of glycerol to absorb water from a hydrocarbon stream.

The procedure involved saturating a sample of refined mineral oil (Clairsol 430, a low viscosity oil used in drilling muds) with North Sea brine, dosing with glycerol and then measuring the time taken for the water to separate from the oil. The final appearance of the oil was also noted. The data obtained are shown in Table 9.

TABLE 9 Water Absorption from Hydrocarbon Using Glycerol

MINERAL OIL (ml)	WATER (ml)	GLYCEROL (ml)	TIME TO SEPARATE (minutes)	FINAL APPEARANCE OF OIL
250	50	0	80	Cloudy - large number of suspended water droplets. No improvement after 4 hours.
250	50	5	25	Cloudy - significant quantity of suspended water droplets visible. No improvements after 4 hours.
250	50	10	15	Slightly cloudy - some water still suspended. No improvement after 4 hours.
250	50	20	10	Clear - only a trace of water left. No improvement after 4 hours.

The results obtained indicate that the addition of glycerol to the oil/water mixture can enhance the rate of separation of the two phases and also reduce the amount of residual water left in the oil phase. This is a strong indication that glycerol could be used to dry a wet gas stream but further work would be required to confirm this.

3.2.2 Corrosion Inhibition Properties of Glycerol/Glycol

A study was undertaken to assess the corrosion inhibition properties of glycerol and glycol.

Solutions of glycerol and glycol (triethylene glycol) in North Sea brine were prepared at 0%, 15%, 25% and 50% by volume of additive. Iron nails (5 cm) were placed into conical flasks containing the test solution (100 ml). The corrosion of the nails was observed over a period of days/weeks/months.

The results obtained are shown in Table 10.

TABLE 10 A Comparison of the Corrosion Inhibition properties of Glycerol and Triethylene Glycol

TEST DURATION (days)	SUBSTRATE CONCENTRATION (% v/v) OBSERVATIONS							
	GLYCEROL				TRIETHYLENE GLYCOL			
	0%	15%	25%	50%	0%	15%	25%	50%
1	TC	TC	NC	NC	TC	TC	TC	TC
2	SC	MC	TC	NC	SC	SC	MC	NC
5	SC	SC	MC	NC	SC	SC	SC	TC
10	SC	SC	SC	NC	SC	SC	SC	MC
20	SC	SC	SC	NC	SC	SC	SC	SC
30	SC	SC	SC	NC	SC	SC	SC	SC
40	SC	SC	SC	NC	SC	SC	SC	SC
220	SC	SC	SC	NC	SC	SC	SC	SC

NC - NO CORROSION

TC - TRACE OF CORROSION

MC - MODERATE CORROSION

SC - SEVERE CORROSION

With neither additive present, the nails exhibited severe corrosion after 2 days in brine. The addition of 15% glycerol partially reduced the extent of corrosion after 2 days but no similar effect was observed with the 15% glycol solution. At an addition of 25% glycerol only a trace of corrosion was observed after 2 days with the equivalent glycol solution giving a moderate corrosion result. On the addition of 50% of either additive no corrosion was observed after 2 days. The 50% glycol solution, however, showed severe corrosion after 20 days, but the nail in the 50% glycerol solution was still clear of corrosion after 220 days.

The glycerol has, therefore, much better corrosion inhibition properties than the glycol and this could make it a more attractive option for use offshore.

A second important feature of the 50% glycerol solution is its freezing point, *ie* less than -30°C (an equivalent triethylene glycol solution froze at -15°C. This implies it could potentially be used as an engine anti-freeze and, unlike glycols, may not require the addition of rust inhibitors. Neat glycerol is a more viscous liquid than either mono- or triethylene glycol, but when all are in aqueous solution they are low viscosity, easily pourable fluids.

3.3 OILSEED RAPEMEAL

3.3.1 Rapemeal as a Chemical Spill Absorbent

A previous, collaborative study involving IOE^[14] indicated that rapemeal was a good general purpose absorbent, and able to absorb its own weight of oil and over twice its own weight of water. The meal also proved to be exceptionally good at absorbing concentrated sulphuric acid, and, depending on its physical form, *ie* powdered or granular, was able to absorb four times its own weight of acid.

In this examination, the meal's absorption capacity toward a range of oilfield chemicals was assessed. The chemicals selected represented a variety of chemical types: acid, alcohol, amine and aldehyde. Information was, therefore, obtained regarding the chemical group absorption efficiency of the meal.

The procedure used involved placing meal (5 g) into a beaker (100 ml). The test fluid was then slowly dripped into the meal (Pasteur Pipette) in fixed portions (1 g) and stirred. The addition of the fluid was continued until the meal was deemed saturated. The results obtained are shown in Table 11.

TABLE 11 Absorption Properties of Rapeseed Meal

TEST FLUID	WEIGHT OF FLUID ADDED (g/5 g of meal)
Hydrochloric Acid (conc)	15
Methanol	4
Triethylene Glycol	5
Corrosion Inhibitor (Quaternary Ammonium)	11
Gluteraldehyde	12
Demulsifier (Phenol Resins)	4
Water*	12
Crude Oil*	4
Sulphuric Acid*	20

* Data from previous study^[14]

To a greater or lesser extent the meal was able to absorb all of the fluids used. The acids, hydrochloric and sulphuric, were very effectively absorbed, with the meal able to absorb three to four times its own weight of acid.

The alcohols, methanol and triethylene glycol, were less efficiently absorbed, but the meal was still able to absorb its own weight in alcohol.

The corrosion inhibitor, a quaternary ammonium compound, and the gluteraldehyde were effectively absorbed, with the meal showing an uptake of twice its own weight.

The demulsifier, a phenol-formaldehyde resin based compound, gave a level of absorption similar to the alcohols and crude oil, *ie* the meal was able to absorb just under its own weight of this fluid.

The meal, therefore, exhibits good overall absorption properties and was able to absorb a broad range of chemical types. The previous study carried out^[14] indicated that rapemeal was a better absorbent than a commercially available material produced from Fullers Earth and there is every reason to assume that this will also be the case for the offshore chemicals. This implies that this material could be used as a 'universal absorbent', and hence only one material would be required to control and remove any spillage on an offshore platform.

3.3.2 Oilseed Rapemeal as a Fluid-Loss Additive in Oil-Based Drilling Muds

As described previously, oil-based drilling muds are emulsions. Certain rock formations are extremely hygroscopic and, when being drilled, can 'draw' the water out of the drilling mud emulsion. This water-loss, described by the industry as fluid-loss, results in a deterioration in the properties of the drilling mud and concomitant reduction in drilling efficiency. A number of proprietary 'chemical packages' are available (fluid-loss additives), which are added to the mud to inhibit water-loss into a dry formation. These additives are based on a range of chemistries, including: starch, cellulose, synthetic polymers, asphaltics, sulphonates, clays and amides.

The additives are often powders and, therefore, it was decided to investigate if ground, sieved rapemeal (1 mm max particles) possessed any fluid-loss properties.

A sample of rapemeal was sieved through a 1 mm screen thus producing a fairly fine powder.

Replicate samples of an oil-based mud were prepared and into these were added increasing quantities of the sieved meal. The quantities of meal used reflected the typical concentrations of fluid-loss additives used offshore. For comparison, a commercially available product based on a synthetic polymer (a polyacrylate), was also included.

Fluid-loss measurements are generally carried out at 120°C in a pressure cell at 500 psi differential pressure. The formulated drilling mud is placed into the cell, heated and pressurised. The volume of fluid 'forced' out of the mud over a thirty minute duration is recorded.

The composition of the mud used, the concentration of meal added, the muds' rheological properties and their fluid-loss characteristics are shown in Table 12 and 13. The fluid-loss measurements were carried out by Schlumberger Dowell Ltd, St Austell.

TABLE 12 Composition of Mud

MUD COMPONENT	QUANTITY (g)
Oil	162.9
Emulsfier	10.0
Clay	7.0
Lime	6.0
Calcium Chloride	30.3
Water	88.06
Barite	115.9

TABLE 13 Fluid-Loss Characteristics of Rapemeal

MUD PROPERTY	QUANTITY OF RAPEMEAL (g)							COMMERCIAL PRODUCT (1 g)
	0	2	4	6	8	10	12	
Plastic Viscosity (cP)	30	30	29	27	29	30	26	27
Yield Point (lb/110 ft ²)	10	10	10	12	10	10	10	15
Gel Strength (lb/110 ft ²)	9	8	6	8	7	9	9	9
Fluid Loss (ml)	4.4	3.6	5.6	5.4	4.0	4.8	5.4	2.2

The mud sample with no added meal gave a fluid-loss result of 4.4 ml. The addition of 2 g of meal appeared to improve this, *ie* to 3.6 ml. The commercially available product significantly improved the situation and gave only 2.2 ml of fluid. Increasing the level of meal added gave no apparent improvement on the fluid-loss situation.

It was also noted that at even high levels of added meal there was very little effect on the viscosity, yield point or gel strength of the mud compared to the sample with no additive. This implies that the meal cannot be used as a viscosity modifier for oil-based drilling muds.

In summary, therefore, at 2 g of added meal some improvement in fluid-loss characteristics, compared to the additive-free mud, was observed. No repeat data were available, however, and therefore it is impossible to conclude if this result represents a real improvement or just an experimental data 'spread'.

At increasing levels of meal there was no apparent improvement in the fluid-loss outcome.

4 CONCLUSIONS

The offshore oil and gas industry provides a huge market for chemicals (100,000-400,000 tonnes per annum). Current environmental legislation is constantly forcing offshore operators to seek out new and ecologically less damaging materials and it must be assumed that regulatory constraints in the future will be even greater. Further, it is likely that health and safety legislation, *eg* governing the control of volatile organic carbon, or the presence of flammable materials on installations, will also become more rigorous.

The low aquatic toxicity and biodegradability of rapeseed oil, its low volatility, high flashpoint and chemical versatility, make it an ideal base material for the formulation of several chemicals

currently used offshore and also for future developments in this ecologically responsive and safety conscious industry.

Oilseed rape comprises a range of material types, *ie* oil, meal and straw. These components can be used unmodified, *eg* as a drilling mud base oil or chemical spill absorbent, or after manipulation, *eg* hydrolysis, as chemical intermediates and end-products, *eg* fatty acids, esters, amines and amides.

Chemical usage by the oil and gas industry can be broken down into two activities, drilling and production. Drilling operations consume the largest quantities of chemicals (of the order of several hundred thousand tonnes per annum), and although the bulk of these comprise inorganic salts, particularly baryte, which cannot be replaced, a significant proportion of the remaining chemicals could well be substituted with oilseed rape derived products. The production chemical market is smaller, being in the order of 20,000 tonnes per year, but the nature of many production chemicals, the demulsifiers, de-oilers and corrosion inhibitors for example, where surface active properties are required, probably make this a more readily accessible market for oilseed derived materials.

This current study has uncovered several new potential areas for oilseed based products including:

- (i) a drilling mud emulsifier, which was found to outperform a commercially available product;
- (ii) an oil spill emulsion breaker, which was able to 'break' a broad viscosity range of emulsions, and which performed as well as a high efficiency commercial product;
- (iii) a combined gas drying agent and anti-freeze with inherent corrosion inhibition properties;
- (iv) corrosion inhibitors based on fatty acid derivatives;
- (v) a general purpose chemical spill absorbent, capable of absorbing the chemical types, *eg* acids, alcohols and hydrocarbons, routinely used or encountered offshore.

Oilseed rape has proven to be a suitable starting material for a range of oilfield chemicals, and coupled with its environmentally benign nature and its good health and safety characteristics, make it an ideal resource for developing products which will meet the increasingly rigorous standards set by the oil and gas industry.

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