

copolymer 3 having a number average molar mass of $\bar{M}_n = 38\,400$ g/mol and a content of methyl acrylate of 55 wt % were compared to measurements on a fourth copolymer with the same composition but a higher \bar{M}_n of 45 000 g/mol, a higher pressure at the cloud point resulted with the high molecular weight polymer.

The distribution of the third component, methyl acrylate, between the phases is a result of a geometric as well as of an electric factor. The geometric factor is governed by the shape and the size of the molecules, whereas the electric factor is determined by the polarity. Methyl acrylate is only a weak polar component. On the other hand, the shape and size of its molecules are similar to those of ethylene. Thus, one would expect the higher concentration of methyl acrylate in the light phase as it has been observed in the experiments.

In order to avoid a gross fouling in the polymerization reactor, the reactor pressure should be above 180 MPa.

Such high pressure should be selected with respect to a lower temperature of the reactor internals after a prolonged shutdown.

Registry No. $\text{H}_2\text{C}=\text{CH}_2$, 74-85-1; $\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3$, 96-33-3; $(\text{H}_2\text{C}=\text{CH}_2)(\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3)$ (copolymer), 25103-74-6.

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Regeneration of Ion-Exchange Resin in Nonaqueous Media

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By use of pyridine in xylene as a model system, it is shown that a cationic exchange resin can effectively remove nitrogen compounds from hydrocarbon oils. The pyridine laden resin can then be regenerated directly with anhydrous HCl dissolved in the oil without switching to an aqueous system. This method is based on the fact that anhydrous HCl when dissolved in the oil dissociates slightly to yield protons which then exchange with resin-bound pyridine ions to form an insoluble salt. The insoluble salt is then flushed out of the system. Cationic resins because of their high loading capacity can be used more advantageously than clays to remove nitrogen compounds from lube oils and distillates and thus improve their thermal and storage stability. The simple resin regeneration technique described here lends itself to technically and economically viable commercial processes for the treatment of petroleum products.

Ion exchangers, particularly those based on synthetic resins, have found wide commercial applications, such as in water softening and deionization, purification of sugar, formaldehydes and antibiotics, uranium extraction, and waste treatment. More potential applications are being discovered. In these applications, ionic or organic impurities in the aqueous media are adsorbed on the resins by way of ion exchange. The ion-exchange resins loaded with bonded ions are then effectively regenerated with counterions for further reuse.

Numerous patents describe the use of ion-exchange resins to purify and stabilize petroleum products (Abrams and Benezra, 1967). Removal of basic nitrogen compounds from lube oils improves their color and thermal stability. Nitrogen compounds are also poisonous to catalysts used for catalytic cracking and hydrocracking. In addition, they contribute to NO_x emission when the fuel is burned. It has been found that cationic exchange resins can be used to remove such nitrogen compounds advantageously owing to their high treating capacity. Most of these applications, however, have not progressed beyond laboratory use. One of the problems in commercializing such a process is the difficulty involved in regeneration of loaded resin. Current techniques for resin regeneration utilize aqueous or water-soluble solution, and the attendant problems resulting from the need to switch between aqueous and organic cycles make the process cumbersome and expensive.

To overcome this problem, we have investigated various regeneration techniques. The results of a direct regener-

ation of a cationic resin in a nonaqueous medium are reported in this paper.

Approach of This Study

The conventional procedure for regenerating ion-exchange resins loaded from an oil medium is cumbersome. Upon exhaustion of the cation-exchange loading capacity, the column is flushed with a solvent miscible with both water and oil. The aqueous regeneration solution, such as HCl, is passed over the ion-exchange column to elute the adsorbed nitrogen compound contaminants and then flushed with the solvent miscible with both water and oil before reuse. In switching solvents back and forth, the waste streams are generated and have to be treated, leading to an expensive operation. More importantly, the product and solvent can be contaminated in the process.

In this study, a cationic resin loaded with basic nitrogen compounds in oil is regenerated directly by contacting it with an anhydrous acid. The basic nitrogen compounds are replaced from the resin by protons and form an insoluble salt, which is flushed out by an appropriate solvent or by the oil feed itself. In this procedure, switching of solvents can be minimized, leading to an efficient operation (Yan and Shu, 1984).

Experimental Section

The cationic exchange resin used was Amberlyst 15 in acid form. This resin is of the macroporous type and made

Table I. Pyridine Loading Capacity of Regenerated Resin^a

regeneration method	regeneration cycle	loading capacity, mequiv/g
A	3	1.7
A	5	1.7
A	6	1.8
B	3	1.8
C	5	1.4

^a Resin: Amberlyst 15. Ion-exchange capacity: 4.6 mequiv/g (by NaOH).

of sulfonated styrene-divinylbenzene. The ion-exchange capacity determined by sodium hydroxide titration was 4.6 mequiv.

Pyridine in xylene was used as a model system to simulate nitrogen compounds in lube oils and distillates. The testing solution was prepared by dissolving 10000 ppm (0.124 mequiv/cm³) of pyridine in xylene of C.P. grades.

Two to five grams of resin was packed in a column. For loading, the testing solution was pumped upflow through the column at 0.6 bed vol/min. The effluent was analyzed for pyridine which had leaked through to construct the loading curve. The loading capacity, *C*, is calculated by

$$C \text{ (mequiv/g)} = \frac{T - L}{R}$$

where *T* is the total pyridine charged (mequiv), *L* is the pyridine leaked (mequiv), and *R* is the resin in the column (g).

Having loaded to its exchange capacity, the ion-exchange resin was regenerated. The regenerated resin was reloaded for the next cycle.

Three regeneration procedures were tested.

1. Procedure A. The loaded column was flushed successively with 3 bed vol each of xylene, CH₂Cl₂, and CH₃OH at 0.6 bed vol/min. The flushed column was regenerated with 3 bed vol of 1% HCl in CH₃OH. The regenerated column was made ready for the next cycle by flushing successively with 3 bed vol of CH₃OH, CH₂Cl₂, and xylene. This procedure is a typical regeneration technique and served as the control.

2. Procedure B. Upon finishing the loading cycle, anhydrous HCl was bubbled through the column until substantial breakthrough of HCl took place. Oil-insoluble pyridine salt was formed, leading to turbidity. The column was drained and flushed with 3 bed vol of CH₂Cl₂ to get ready for the next cycle of loading. Methylene chloride is a good solvent for the pyridine salt and can be readily stripped from the resin.

3. Procedure C. This procedure is similar to procedure B, except that tetrahydrofuran (THF) was used as the solvent instead of CH₂Cl₂. THF is a good solvent for pyridine salt and can be stripped from the resin with steam.

The pyridine contents in the solutions were determined by titration using 0.1 N HCl. An automatic pH meter was used for titration to the end point of pH 4.1 determined from the titration curve of 0.124 N pyridine vs. 0.1 N HCl.

Results and Discussions

Loading curves are constructed by plotting pyridine leakage against bed volume of the loading solution. Typical loading curves are shown in Figure 1. The loading capacities of resins after various times of regenerations are shown in Table I.

1. Removal of Pyridine from Xylene. The loading curves (Figure 1) indicate that the cationic resin, Amberlyst 15, is effective in removing pyridine from xylene. Before

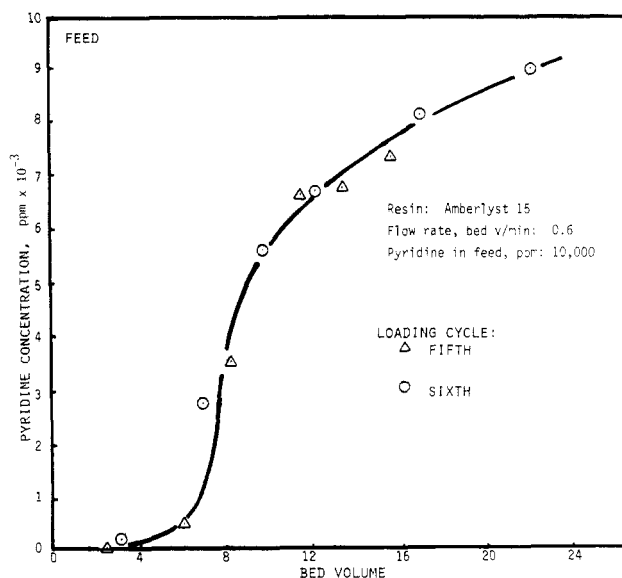


Figure 1. Pyridine loading curve.

pyridine breakthrough, the pyridine concentration was low and the breakthrough curve was sharp. We believe that the efficiency of pyridine removal could have been improved by optimizing the bed configuration, i.e., *L/D* ratio of the column, and operating at a lower flow rate than 0.6 bed vol/min.

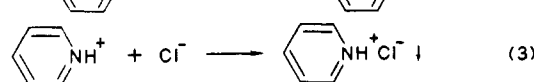
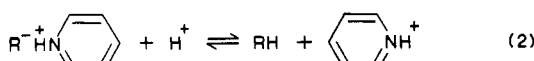
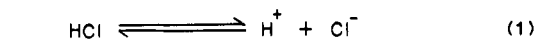
2. Loading Capacity. The loading capacities of pyridine from xylene were consistently about 1.7 mequiv/g (Table I), which were significantly lower than those determined by NaOH titration. The adsorption of organic base from a nonaqueous media is often lower than expected. For example, Saunders (1957) found that the maximum equilibrium absorption of quinine is only one-fifth of the available carboxyl group, as determined by sodium hydroxide absorption. The low apparent absorption capacity could be due to its slow absorption rate resulting from low dissociation and the large size of the molecule. The exchange rate with an amine and a strongly acidic resin is slower by a factor of 1000–2500 in anhydrous solvents such as benzene and alcohols than in water (Vermeulen and Huffman, 1953). The high flow rate used in this study undoubtedly contributed to the apparent low loading capacity.

The loading capacities of cationic resins are much higher than those of conventional clays. If the concentration of nitrogen compounds is 100 ppm, each gram of resin with 1.7 mequiv/g loading capacity can treat about 200 g of oil. The treating capacity of clays is typically 2–5 g of oil/g of clay.

3. Efficacy of Direct Regeneration. Direct regeneration of loaded resin with anhydrous HCl is as effective as the conventional technique using aqueous regeneration solution. This is evident from the measurements of the loading capacity of resins regenerated by using procedures B and C being comparable to the control procedure A (Table I). The loading capacities of the regenerated resin remained constant after six cycles of regeneration. These results suggest that direct regeneration with an anhydrous acid is technically viable.

Gemant (1962) found that if strong acids such as hydrochloric acid and trichloroacetic acid are dissolved in hydrocarbon solvents, there exists a finite concentration of hydrogen ions as a result of electrolytic dissociation. The dissociation constant varies with the dielectric constant (*D*) of the solvent and varies from 10⁻²⁰ to 10⁻¹⁶ in a range of *D* from 2.4 to 2.6.

The ion exchange on the resin involves the interaction between the generated proton (eq 1) and the pyridinium ion on the resin (eq 2). The pyridinium ion is displaced



from the ion exchange and then diffuses into the solution and reacts with Cl^- to form the pyridinium salt (eq 3). The pyridinium salt is not very soluble in xylene and precipitates out, leading to the observed turbidity.

Even though the degree of dissociation of HCl is small (eq 1), the equilibrium is shifted by ion adsorption (eq 2), and the originally undissociated HCl molecules are subsequently also adsorbed. This mechanism is similar to the case in which a weak acid, such as acetic acid in water, is brought in contact with an OH-type anion exchanger. The formation of insoluble pyridinium salt (eq 3) assures the technical feasibility of complete exchange of pyridinium ion from the resin.

This technique of direct regeneration of cationic resins with HCl in nonaqueous media is general and should be applicable to other ion exchangers.

To demonstrate the principle in the procedures described, solvents were used to dissolve and flush the pyridinium salt from the regenerated resin. It should be apparent that the insoluble pyridinium salt could be flushed out with the hydrocarbon itself in a form of a fine suspension without the use of an additional solvent. The pyridine in the spent eluate can be readily recovered as product by extraction with a solvent, such as water, leading to a simple and environmentally sound process.

Summary

The nitrogen compounds in hydrocarbon oils can be removed effectively with cationic exchange resins. The treating capacity of the resin is much higher than the conventional clay.

The resin loaded with nitrogen compounds can be directly regenerated with an anhydrous acid dissolved in the hydrocarbon oil without switching to an aqueous system. The overall mechanism is based on the fact that the acid dissociates to yield protons which exchange with and replace the pyridinium ions on the resin; these pyridinium ions then form insoluble pyridinium salt with Cl^- . This mechanism is similar to the ion exchange of weak acid in water with an anion exchanger.

The direct regeneration technique described here is simple and environmentally sound and lends itself to commercial applications.

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Registry No. HCl, 7647-01-0; pyridine, 110-86-1; xylene, 1330-20-7.

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Characterization Parameters for Petroleum Fractions

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A generalized empirical correlation has been proposed to predict physical properties of pure hydrocarbons and undefined petroleum fractions. Properties such as critical temperature (T_c), critical pressure (P_c), critical volume (V_c), molecular weight (M), normal boiling point (T_b), specific gravity (S), refractive index (n), carbon-to-hydrogen weight ratio (CH), and heat of vaporization (ΔH_v) may be predicted from any pair of available characterizing parameters (T_b , S), (T_b , I), (T_b , CH), (M , S), (M , I), (M , CH), (ν_1 , S), (ν_1 , I), or (ν_1 , CH) as input parameters. Proposed correlations are generally superior or at least equivalent to the existing correlations and are applicable in the molecular weight range 70-300 and normal boiling point range 80-650 °F.

Background

Riazi (1979), reported by Riazi and Daubert (1980), developed a simple two-parameter equation for prediction of physical properties of undefined hydrocarbon mixtures of the form

$$\theta = aT_b^b S^c \quad (1)$$

where θ is the property to be predicted, T_b is the normal boiling point (°R) and S is the specific gravity at 60/60 °F. Properties such as molecular weight, refractive index, critical properties, density, and heat of vaporization were successfully correlated to T_b and S through eq 1. This

equation was comparable to similar correlations such as those of Kesler and Lee (1976) and was included in API *Technical Data Book—Petroleum Refining* (1986) for predicting the molecular weights, refractive indexes, and pseudocritical temperatures and pressures of undefined mixtures.

This form of correlation was later used by other investigators; for example, Gray (1981) used the form of eq 1 for the molecular weight of coal liquids. Most recently, Riazi and Faghvi (1985) used the form of eq 1 for prediction of thermal conductivity of liquid and vapor hydrocarbon systems.