

API SOIL & GROUNDWATER RESEARCH BULLETIN

*A summary of research
results from API's Soil
and Groundwater
Technical Task Force*

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Selective Subcritical Water Extraction of Aromatic and Aliphatic Organic Pollutants from Petroleum Industry Soils and Sludges

Summary

The unique properties of subcritical water were investigated in a laboratory study for their ability to selectively remove different organic compound classes from petroleum wastes and petroleum products. Class-selective extractions of phenols alkylbenzenes, Polyoynuclear aromatic hydrocarbons, and alkanes from a catalyst and a tank bottom sludge were achieved by simply changing water temperatures (50 to 300°C) or pressures (5 to 50 atm). Nearly complete (>90%) removal of hazardous organics (e.g., PAHs) from a hydrocarbon sludge was achieved while extracting very little of the non-hazardous organics. The effect of water temperature on partitioning of BTEX and PAHs from gasoline and diesel fuel to subcritical water was also determined, and the results suggest that subcritical water may be useful to reduce benzene content in gasoline. Compared to supercritical water (T>374°C, P>218 atm), subcritical water is much less corrosive to equipment, a particular advantage for large scale applications. Further research is needed to evaluate performance and cost in pilot scale treatment systems.

Introduction

Supercritical fluids have received much attention for analytical and processing applications. In particular, supercritical carbon dioxide has been used to extract relatively non-polar organics from a variety of environmental matrices, and has also been used for chemical processing. While supercritical carbon dioxide is relatively unreactive and is not an efficient solvent for polar organics, supercritical water is highly reactive and an excellent solvent for polar and non-polar organics. However, the extreme conditions required (T>374°C, P>218 atm) and the high reactivity of supercritical water have limited its use almost exclusively to the destruction of very hazardous materials (e.g., nerve gas agents).

In contrast to the large amount of research and numerous industrial applications involving super-

critical carbon dioxide and supercritical water, very little use of so-called "subcritical" water has been made. [Note that "subcritical" water is a non-specific term that has gained general acceptance. The conditions referred to in this report are better described as superheated water (i.e., water held above the normal boiling point with enough applied pressure to maintain the liquid state)]. This is surprising since subcritical water has several potential physiochemical as well as practical advantages over supercritical water and supercritical carbon dioxide. As shown in Table I, the polarity (solvent strength) of subcritical water can be controlled over a much broader range than either supercritical water or carbon dioxide. By simply controlling temperature with enough pressure to maintain the liquid state, a very wide range of solvent polarity can be achieved with pure water, as

Temperature Influence on Physical Properties of Water

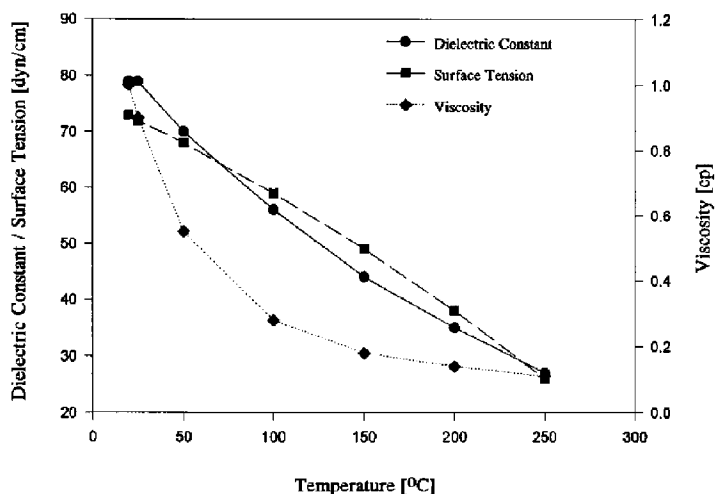


Figure 1: Changes in water polarity (dielectric constant, ϵ) viscosity, and surface tension with temperature under enough pressure to maintain the liquid state.

demonstrated in Figure 1. Note that water's polarity can be controlled from very polar ($\epsilon = 80$) to polarities associated with common organic solvents such as methanol and acetonitrile.

In addition to changing the polarity of water, increasing temperature also lowers the viscosity and surface tension of water — both factors that enhance water's ability to extract organic compounds from contaminated solids (Figure 1). For example, raising the temperature of liquid water to 250°C lowers its surface tension from 0.89 cp (at ambient temperature) to 0.11 cp. Thus, water is much more able to “wet” surfaces at higher temperatures. In addition, with the same increase in temperature, the viscosity of water decreases dramatically at higher temperatures (Figure 1). Thus, solute mass transfer is enhanced at higher temperatures.

Additional comparisons of subcritical water with supercritical water and carbon dioxide shown in Table I also demonstrate a good potential for using water as a selective extraction fluid. In addition to the physicochemical parameters, subcritical water has practical advantages, including much lower temperature and pressure requirements for non-

polar organic extractions than supercritical water. A particular advantage for large scale applications is the much lower corrosivity of subcritical water compared to supercritical water. In these experiments, stainless steel is a reliable material for subcritical water extraction containment. Supercritical water extraction requires exotic (and expensive) materials to avoid corrosion.

Applications of Subcritical Water Extraction for Removing Hazardous Organics from Contaminated Solids

Example 1: Extraction of Phenols, PAHs, and Alkanes from a Waste Sludge

The ability of subcritical water to selectively extract different classes of organic pollutants from sludges and a catalyst was determined using a laboratory-scale extraction system which allowed collection of the extracted organics for analysis by GC/MS. Quantitative comparisons were made versus conventional organic solvent extractions. The effects of temperature and pressure were evaluated. In addition, some samples were extracted with steam (by simply lowering the pressure) after subcritical water extraction.

A petroleum waste sludge was extracted at several temperatures to determine the selectivity and efficiency of extraction for different contaminant compound classes. As shown in Table II, phenols were efficiently extracted in 15 minutes using only 100°C subcritical water, while only the lowest molecular weight PAH, naphthalene, showed significant extraction. However, when the temperature was raised to 250°C (sequentially after the 100°C extraction), the PAHs were quantitatively extracted. Note also that all of the alkanes (except dodecane) remained at least 90% on the sludge. The results in Table II clearly demonstrate the potential for using subcritical water to remove hazardous organics (e.g., phenols and PAHs) from waste sludges without extracting non-hazardous components (e.g., the alkanes). Since the phenols and PAHs were completely removed from the sample, but only ~ 1 wt% of the total sample was extracted, these results suggest that subcritical water could be used to drastically reduce the volume of hazardous sludges. Finally, when the same sample was sequentially extracted with steam at 250°C, all alkanes were quantitatively removed.

Example 2: Extraction of PAHs from a Catalyst

The extraction of a spent processing catalyst is shown in Table III. The first extractions were performed at 250°C, since that condition was successful in removing PAHs from the soil and sludge, as discussed above. However, the removal of PAHs from the spent catalyst was not efficient in 15 minutes at 250°C. Therefore, the extraction temperature was increased to 300°C. Higher removal of the PAHs was achieved (Table III), but the removal was still incomplete. Since the catalyst was in pellets with much larger particle sizes than the soil or sludge, slow mass transfer was suspected of limiting the extraction rate. Therefore, additional extractions were performed at 300°C for 60 minutes. As shown in Table III, the longer extraction did yield much better removals, demonstrating that the extraction rate could be limited by the large catalyst particle size. The particle size limitation was confirmed by grinding a fresh catalyst sample, and extracting at 300°C for 15 minutes.

The high removals obtained in 15 minutes with the ground catalyst clearly demonstrates that the extraction of the PAHs was limited by the poor mass transfer in the large catalyst particles. However, efficient removal of the PAHs can be achieved either by a long (60 min) extraction time, or by reducing the catalyst particle size.

BTEX and PAH Partitioning Between Fuel and Water

In addition to the extraction of organics from solids, initial experiments were performed to determine the ability of subcritical water to perform selective extractions in liquid/liquid systems. The first experiment was to determine the effect of water temperature on the solubility of toluene. A method and apparatus were developed to allow the determination of solubilities in subcritical water up to 200°C and pressures up to 300 atm. As shown in Figure 2, the solubility of toluene increases from 540 ppm at 21°C to nearly 13,000 ppm at 200°C, an increase of ~ 23-fold.

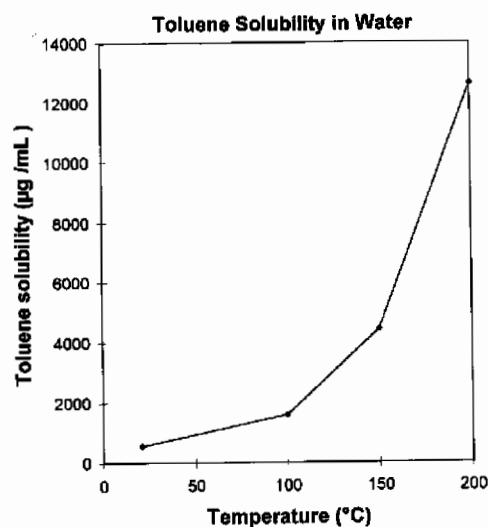


Figure 2: The effect of temperature on the solubility of toluene in subcritical water at 50 atm.

Since toluene's solubility increases dramatically with temperature in subcritical water, and since alkanes were difficult to extract in previous examples (indicating low solubility), additional experiments were conducted to determine the relative partitioning of benzene, toluene, ethylbenzene and xylenes (BTEX) between gasoline and water (1:2 ratio). When gasoline was equilibrated with subcritical water, the fraction of each BTEX component in water increased substantially. For example, the fraction of benzene found in the water phase increased by more than 10-fold when the water was heated to 200°C. In contrast, non-aromatic compounds, such as the alkane components of gasoline, showed no significant partitioning into water regardless of the water temperature as demonstrated by the results for n-octane in Figure 3. Similar results were obtained for PAHs from diesel fuel. These results suggest that partitioning of fuels with subcritical water may be a viable method for selectively removing aromatic hydrocarbons (e.g., benzene) from the bulk fuel.

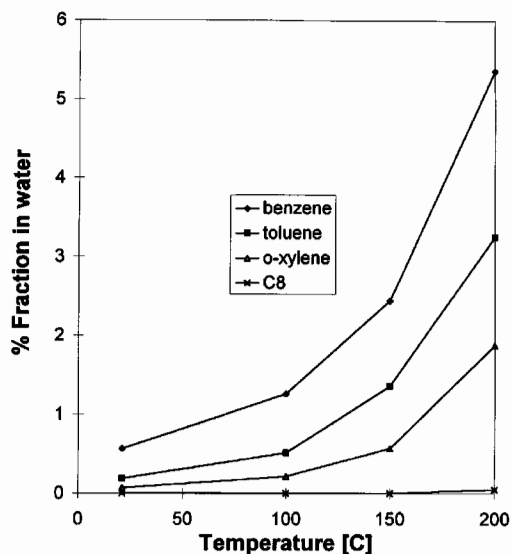


Figure 3: The effect of temperature on the partitioning of BTEX compounds from gasoline into subcritical water at 50 atm.

Future Research

Areas suggested for future studies to evaluate the potential uses of subcritical water include:

- Fundamental solubility behavior of hazardous organics and other fuel components in subcritical water at temperatures up to 300°C is needed to support both fundamental understanding of the chemistry involved, as well as to allow process modeling to be performed.
- A better understanding of the thermodynamic and kinetic processes which control subcritical water extraction of hazardous organics from solids is needed to support process development.

Additional Reading

The results of these investigations are reported in detail in the following two publications:

Yang, Y.; Miller, D.J.; Hawthorne, S.B. "Organic Partitioning from Gasoline and Diesel Fuel into Water and Toluene Solubility at Elevated Temperatures and Pressures," accepted for publication in *J. Chem. Eng. Data*.

Yang, Y.; Hawthorne, S.B.; Miller, D.J. "Class-Selective Extraction of Polar, Moderately Polar, and Nonpolar Organics from Hydrocarbon Wastes Using Subcritical Water," *Environ. Sci. Technol.* 1997, 31, 430-437.

Additional information on using subcritical water to extract organic pollutants can be found in the following [references](#):

Yang, Y.; Bowadt, S.; Hawthorne, S.B.; Miller, D.J. "Subcritical Water Extraction of Polychlorinated Biphenyls from Soil and Sediment," *Anal. Chem.* 1995, 67, 4571-4576.

References

Hageman, K.J.; Mazeas, L.; Grabanski, C.B.; Miller, D.J.; Hawthorne, S.B. "Coupled Subcritical Water Extraction with Solid-Phase Microextraction for Determining Semivolatile Organics in Environmental Solids," *Anal. Chem.* 1996, 68, 3892-3898.

Hawthorne, S.B.; Yang, Y.; Miller, D.J. "Extraction of Organic Pollutants from Environmental Solids with Sub- and Supercritical Water," *Anal. Chem.* 1994, 66, 2912-2920.

Table I. Typical Characteristics Related to Organic Pollutant Extractions for Subcritical (Superheated) Water, Supercritical Water, and Supercritical CO₂

	Subcritical Water	Supercritical Water	Supercritical CO ₂
Temperature Range	>25 to 300°C	>374°C	32 to 150°C
Pressure Required	2 to 50 atm	>218 atm	>72 atm
Density Range	0.8 to 1 g/mL	0.1 to 0.6 g/mL	0.3 to 0.9 g/mL
Useful Polarity Range	15 to 85	5 to 15	1 to 2
Corrosivity	Low to Moderate	High	Low
Relative Engineering Costs	Moderate	High	High
Organics Solvated	Polar to Non-Polar	Polar to Non-Polar	Non-Polar
Selectivity	Potentially High	Non-Selective	Some Selectivity

Table II. Selective Extraction of Phenols, PAHs, *n*-Alkanes from Petroleum Waste Sludge

	Cumulative % Extracted			
	Concentration µg/g	Water 100°C, 50 atm	Water 250°C, 50 atm	Steam 250°C, 5 atm
Phenol	1310	94	98	100
o-Cresol	1020	88	97	100
m,p-Cresol	2360	98	100	100
C ₂ -Alkylphenol	750	89	97	100
Naphthalene	1010	45	94	100
Phenanthrene	20	15	92	100
Pyrene	1	4	91	100
C ₁₂	700	6	21	100
C ₁₅	600	5	13	100
C ₁₈	130	6	12	100
C ₂₁	23	<1	4	100
C ₂₄	25	<1	4	100
C ₂₇	58	<1	3	100
C ₃₀	34	<1	<1	100
C ₃₃	9.0	<1	<1	100
Total Alkanes	5125	6	22	100

Table III. 15-Minute Extractions of Organics from Spent Catalyst

	Concentration μg/g	% Removed in 15 min.			
		Original Sample, 250°C, 15 min.	Original Sample, 300°C, 15 min.	Original Sample, 300°C, 60 min.	Ground Sample, 300°C, 15 min.
Naphthalene	31	73	95	100	99
Phenanthrene	165	38	86	99	100
Fluoranthene	14	34	81	98	99
Pyrene	2510	20	84	100	100
Benz[<i>a</i>]anthracene	8.1	15	47	98	100
Chrysene	55	14	62	97	99
Benzo[<i>b+k</i>]fluoranthene	64	12	57	94	98
Benzo[<i>a</i>]pyrene	13	16	47	93	98
Indeno[<i>1,2,3-cd</i>]pyrene	11	11	49	91	94
Benzo[<i>ghi</i>]perylene	91	10	45	90	93

Acknowledgments

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Other Publications of Interest from API

“Characteristics and Performance of Supercritical Fluid Extraction (SFE) in the Analysis of Petroleum Hydrocarbons in Soils and Sludges,” API Publication 4618, May, 1995.

“Compilation of Field Analytical Methods for Assessing Petroleum Product Releases,” API Publication 4635, December, 1996.

“Sampling and Analysis of Gasoline Range Organics in Soil,” API Publication 4516, October, 1991.

“Intralaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils: Diesel Range Organics, Gasoline Range Organics, and Petroleum Hydrocarbons,” API Publication 4599, June, 1994.

“Screening of Soils for Leachable Benzene,” API Publication 4548, December, 1992.

ABOUT API'S SOIL & GROUNDWATER TECHNICAL TASK FORCE...

API's Soil and Groundwater Technical Task Force provides an expert, multidisciplinary technical focal point within API to address soil and groundwater issues. The Task Force identifies and defines emerging technical issues related to soil and groundwater contamination/protection, and develops research programs to address these issues. API-sponsored research yields practical tools and basic science for risk-based, cost-effective solutions to the petroleum industry's soil and groundwater problems. The Task Force disseminates information and research results through publications, presentations, and interaction with industry clients and regulatory agencies.

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