Study of co-solvent effects on stickies removal in supercritical fluid extraction

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ABSTRACT

Using supercritical carbon dioxide to remove stickies in recycling fibers is studied at laboratory scale. Supercritical carbon dioxide is the most environmental friendly supercritical fluid widely used in extraction process. This study includes co-solvent effect on sticky compounds removal by using supercritical carbon dioxide extraction. The sticky compounds are dispensed onto fibers, and then extracted using supercritical carbon dioxide and co-solvent in order to study the efficiency of stickies removal. The results show that supercritical carbon dioxide can remove most sticky compounds such as paraffin wax, polyethylene wax, polyvinyl acetate, polystyrene butadiene. It is demonstrated that with co-solvent, the extraction efficiency increases considerably under the same extraction conditions.

INTRODUCTION

Recycled paper products which contain a variety of sticky compounds bring many problems in recycling pulp and paper mills. The term "stickies" are classified as hot melts used in inks and coatings, pressure-sensitive adhesives, coating binders, wood resins and wet strength agents. The tacky nature of these materials makes the contaminants easy to deposit on forming fabrics, press felts and dryers. Stickies in recycled paper fibers reduce paper quality and cause paper machine down time. Currently, the methods of removing stickies are not sufficient to completely solve the problem.

In this study, the sticky contaminants are categorized as wax, hot-melts and latex [1]. Hot-melts are used in book bonding, ink formulation and coating barriers. The typical compounds in hot-melt adhesives are polyethylene and copolymers, polypropylene and copolymers, and wax. These materials usually have melt point around 60-135℃. Waxes used in packaging are primarily paraffin wax and microcrystalline wax. These petroleum waxes contain straight-chain hydrocarbons from C_{18} to C_{85}. The melt points are in the range of 50-85℃. Coating binders are the second most abundant components in the coating colors other than pigments. Several soft latexes such as polystyrene butadiene latex and polyvinyl acetate latex are widely used as coating binders [2]. The high binding strength of cross linked polymers especially polystyrene butadiene and its copolymers make them hard to be removed by most of organic solvents. Polystyrene butadiene is also the component of ink formula.

Most of the contaminants are soluble in a number of organic solvents. The problems raised by using organic solvents are the costs and environmental pressure. Recently, supercritical fluid extraction has brought more interests in paper recycling. Supercritical fluids have many features that are suitable for process control. It has gained increased attention as a potential replacement for conventional organic solvent extraction [3 ,4 ,5]. The density of supercritical fluids which is an important factor of solubility is sensitive to temperature and pressure. This is a suitable property for process control.

Carbon dioxide is the most common solvent used in supercritical fluid extraction. CO_2 is environmental friendly, nontoxic, nonflammable and inexpensive. It has critical temperature of 31.1℃ and critical pressure 1070 psi, which is easy to achieve. Several experiments have been reported and patented of using supercritical carbon dioxide to remove wax in old corrugated containers and most of the other sticky contaminants. Stauffer et al. [6] reported supercritical CO_2 extraction of paraffin based wax coating from saturated and curtain-coated old corrugate containers. The conditions of their experiment are 4350 psi and 100℃ with a flow rate of 3ml/min extracted for 1 hour. About 70-98% of saturated and curtain-coated waxes were extracted. Kimberly Clark patents [7 , 8 , 9, 10] reported that the extraction efficiency of supercritical CO_2 of most sticky contaminants. The experiment conditions are 4700-5000psi, 66℃ and 74℃ and at a flow rate of 16 standard liter per minute for 3 hours, at a flow rate of 29 standard liter per minute for another 3 hours. The extraction efficiency was between 23-30% for mostly styrene butadiene and polyvinyl acetate compounds.

Although supercritical CO_2 has many favorable feature in extraction, the solubility of strong polar compounds in CO_2 are very low due to the low polarity of CO_2. As been proved theoretically and experimentally, a small amount of polar or non-polar co-solvent can affect the solubility of supercritical CO_2 considerably [11 , 12]. In the present paper, the effect of co-solvent was investigated at laboratory scale in a 30ml volume extractor. Several different co-solvents were selected to study the efficiency of extraction.

EXPERIMENTAL

Materials

Supercritical fluid grade CO_2 was supplied by Airgas, Greatlakes. Cyclohexane, toluene, acetone at HPLC grade were supplied by Acro Organics. Pure polystyrene butadiene with 45% styrene and polyvinyl acetate were from Sigma-Aldrich. Paraffin waxes with modifier were from Honeywell. Hot melt adhesives which contain polyethylene, polypropylene and wax were from H.B. Fuller. These materials were used as received. Styrene butadiene latex with 50% of styrene and polyvinyl acetate latex were from Rohm HAAS and Dow Chemical. 100% softwood fibers were used to disperse the contaminants. Fibers and contaminants were set over 24 hrs before extraction.

Apparatus

The schematic of the experimental setup is shown in Figure 1. It contains the following parts: (1) CO_2 cylinder, (2) compressor and pressure controller, (3) pressure control valve, (4) pressure gauge, (5) extraction cell with heating tape and digital thermometer, (6) decompress valve, and (7) collection chamber.

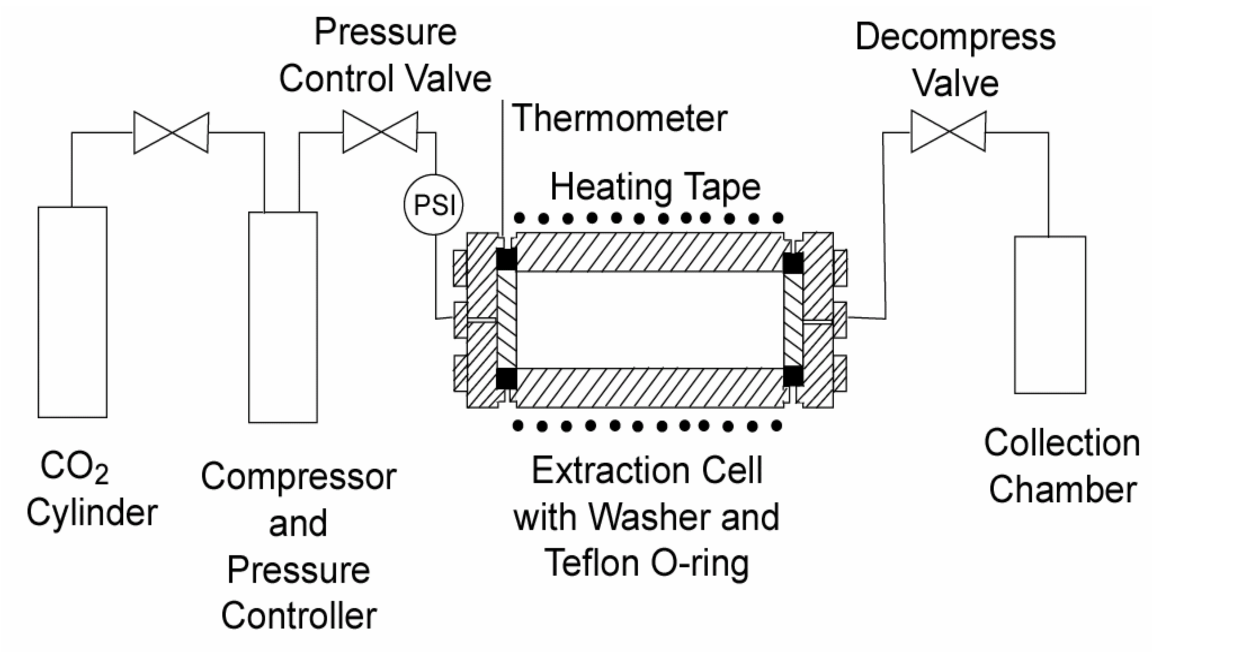

Figure 1: Experimental setup

The pressure controller is ISCO series D, model 260D syringe pump. This pump is used in conjunction with a recirculation chiller to pump CO_2 into extraction cell. Outside of the cell body is wrapped with electrical heating wire. The temperature of the extraction cell is measured by digital thermometer attached to the cell body. The pressure gauge is in pressure range of 0-5000psi.

Experimental Procedure

Before supercritical CO_2 extraction, the solubility of modeling compounds was tested in organic solvents. Cyclohexane was used to solve wax and hot melt compounds. It showed that at room temperature paraffin wax was easy to dissolve in cyclohexane. In heated cyclohexane, hot melt adhesive with mainly polyethylene and polypropylene was soluble. Polyvinyl acetate was able to dissolve in acetone at room temperature. Toluene or chloroform could only swell polystyrene butadiene under room temperature.

CO_2 was pumped to pressure controller which was chilled to 5℃. Every load was 80mg of one compound. After filled the extraction cell with CO_2, the cell was heated to the desired temperature. The pressure controller can further control the pressure inside the extraction cell. Compounds were cut in small pieces before loaded into the extraction cell. The extraction was conducted for 1 hour with no CO_2 flow rate control. Then the decompressing valve was opened to decompress, at the same time the extracted compounds were collected in collection chamber. To completely recover the solute, the extraction cell was flushed out by carbon dioxide for one minute. The pre-weighted collection chamber was weighted again to measure the amount of compounds extracted. By means of the measured solute mass, the solubility value was calculated.

Paraffin wax was used to optimize the process condition. By combining different pressures and temperatures, the optimized pressure and temperature were set for all compounds to compare the extraction efficiency.

Fibers with dispersed compounds were cut in 1mm strips and loaded. The extraction conditions were kept constant during the different compound extractions. Co-solvent selections were based on organic solvents tested at room temperature. 5% of co-solvent in volume was preloaded before pumping CO_2 into the extraction cell.

RESULTS AND DISCUSSIONS

Binary System (Carbon Dioxide/Compounds)

Paraffin wax was used to study the effects of pressure and temperature in extraction. As expected, with increasing the temperature and pressure, it showed an increased solubility of paraffin wax in supercritical carbon dioxide (Table 1).

Temperature (^oC)	40-42	40-42	65-70	92-97
Pressure (psi)	2400-2500	4500-4750	4000-4250	4000-4250
Efficiency (%)	14	25	62.5	87.5

Table 1: Solubility of paraffin wax in a binary system

At the constant condition of temperature between 92-100 ^oC and pressure between 4500-4750 psi, other compounds were tested. The results are listed in Table 2.

Compounds	Parafin wax	Hot-melt adhesive	PVAc	Polystyrene Butadiene (45% of styrene)
Efficiency (%)	87.5	25	12.5	1

Table 2: Solubility of sticky compounds in a binary system

Because of the low polarity of carbon dioxide, the sticky compounds which have high polarity showed low solubility in supercritical carbon dioxide. Polystyrene butadiene which has an aromatic ring showed the lowest extraction efficiency in pure supercritical carbon dioxide.

Ternary System (Carbon Dioxide/ Compounds/ Co-solvent)

In the case of ternary system, the operating pressure and temperature were chosen as same as in the binary system extraction. The solubilities of sticky compounds in supercritical carbon dioxide with 5% co-solvent in volume were presented in Table 3.

Compounds dispersed on fibers	Paraffin wax	Hot-melt adhesive	PVAc	Polystyrene Butadiene (45% of styrene)
Co-solvent	Cyclohexane	Cyclohexane	Acetone	Toluene
Efficiency (%)	97.5	44	47.5	12.5
Co-solvent effect	1.11	1.76	3.8	12.5

Table 3: Solubility of sticky compounds in a ternary system

Compared to Table 2, the increasing of solubility was clearly shown. In the table, the co-solvent effect was calculated as the ratio of solubility in presence of a co-solvent to that with absence of a co-solvent. As shown in Table 2, these are larger increasing in polar compounds solubility than non-polar compounds. The polar co-solvent acetone and toluene increase the local density of cosolvent-CO_2 mixture surrounded the sticky compounds. This density increasing contributed to the increasing of solubility. On the other hand, the polarity of polar compounds and polar co-solvents played an important role in co-solvent effect. The strong attractive polar interactions between compounds and co-solvent resulted in the enhanced solubility. This can explain the higher co-solvent effect of polar co-solvent acetone and toluene on polar compounds like styrene butadiene. Cyclohexane is non-polar co-solvent which showed limited increasing of solubility.

Quaternary System (Carbon Dioxide/Co-solvent/Compounds/Fibers)

In order to study the extraction of sticky compounds in fibers, a quaternary system with carbon dioxide, co-solvent, sticky compounds and fibers was conducted. Under the same operating conditions as in a ternary system, the solubilities were listed in Table 4.

Compounds dispersed on fibers	Parafin wax	Hot-melt adhesive	PVAc	Polystyrene Butadiene (50% of styrene)
Co-solvent	Cyclohexane	Cyclohexane	Acetone	Toluene
Efficiency (%)	93.8	43	45	22.5

Table 4: Solubility of sticky compounds in a quaternary system

In a complex quaternary system, the interaction of every component in the system is hard to evaluate. It was surprised that polystyrene butadiene showed the highest co-solvent effect in this quaternary system. The effect maybe contributed by the hydroxyl groups in fibers.

The density of supercritical fluid is an important factor for extraction efficiency. With decreasing temperature, the fluid density is increasing at certain pressure. Polystyrene butadiene (50% styrene) in a quaternary system was extracted at the same pressure as previous studies with lower temperature to increase the density of supercritical fluid. The extraction efficiency increased about 5% at temperature of 65-70 ^{o}C. The control of pressure and temperature in a system with co-solvent needs to be optimized for further study.

CONLUSIONS

The solubility of sticky compounds in pure supercritical carbon dioxide and with co-solvent was investigated at pressure ranging from 4500 psi to 4750 psi and at temperature ranging from 92 ^{o}C to 100 ^{o}C. It was found that co-solvent greatly enhanced the solubility of sticky compounds in supercritical carbon dioxide. Especially for polar compounds, the polar co-solvent increases the solubility by increasing the local density of co-solvent-CO_2 mixture surrounded the solute. The solubility of compounds in supercritical carbon dioxide and co-solvent is also sensitive to the operating pressure and temperature. It was illustrated that polar co-solvent had better co-solvent effect than non-polar co-solvent for polar contaminate compounds. The selection of polar co-solvent could be the means to enhance the extraction efficiency.

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Contents

Typical Stickies

- Hot melt adhesives
  - Vinyl acetate polymer and copolymer
  - Polyethylene, polypropylene
  - Wax
- Coating binders
  - Various types of soft lattices
    - Styrene butadiene
    - Polyvinyl acetate
- Wax
  - Paraffin wax
  - Microcrystalline wax

Sticky Compounds in This Study

- Polystyrene butadiene with 45% styrene from Aldrich, polystyrene butadiene latex (SB Latex) with 50% styrene from Rohm HAAS company
- Polyvinyl acetate from Aldrich, polyvinyl acetate latex (PVA Latex) from Rohm HAAS company
- Hot melt adhesives contains polyethylene co-polypropylene and wax from H.B. Fuller
- Paraffin wax (100%, no modifier) from Honeywell

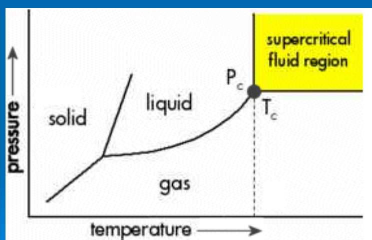
Supercritical Fluids Extraction

- Characteristic features
  - Sensitivity to temperature and pressure near the critical region
  - Supercritical fluids have both liquid and gas like properties
  - Process flexibility
  - Environmental perspective: reduce the usage of organic solvent

Supercritical Carbon Dioxide

- A common solvent for supercritical fluid extraction
- It is nontoxic, nonflammable, easy to obtain and very convenient critical temperature and pressure
- Critical temperature T_c=31℃ and critical pressure P_c=1070psi

Phase Diagram



Reports in Recycling Fibers Using Supercritical CO_2 Extraction

- Kimberly-Clark patents of removing stickies
  - Removed 25% to 30% styrene butadiene and polyvinyl acetate with no co-solvent in a 3 liter extraction vessel
  - Pressure 4700-5000 psi, temperature 66℃-74℃, extraction time 6 hours
  - Semi-continuous reaction at 16-29 slpm/gm (34gm CO_2/gm sample)
- North Carolina State University-removing paraffin wax from OCC
  - 70% to 98% of extraction efficiency for OCC with no co-solvent in a 3ml vessel and a 500ml vessel
  - Pressure 4350 psi, temperature 100℃, extraction time 1 hour
  - Semi-continuous reaction at 36-67gm CO_2 /gm sample, 3ml/min

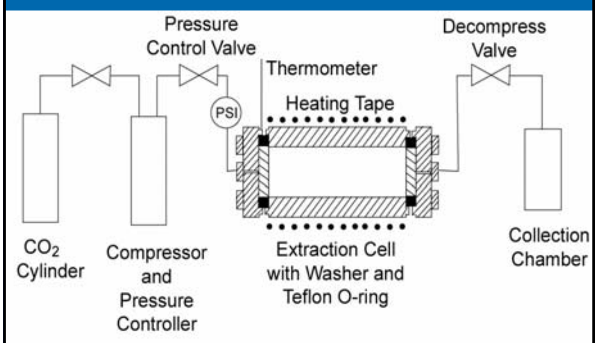
Limitations of Supercritical CO_2 Extraction

- The low polarity of CO_2 limits its solubility
- The solubility of many strong polar compounds in supercritical CO_2 is very low
- A very high operating pressure would be required
- A remarkable solubility enhancement can be achieved by adding 5% polar co-solvent to increase the solubility of polar compounds

Lab Scale Supercritical CO_2 Extraction System Built for This Study

- The system consists:
  - Compressor
  - Heater
  - Extraction vessel
  - Pressure control valve
  - Decompress valve
  - Collection chamber
- 30 ml batch reactor, no CO_2 flow rate control

Scheme of Extraction Equipment



Experiment Design

- Organic solvent solubility
- Pure supercritical CO_2 extracts compounds only
- Supercritical CO_2 with co-solvent extract compounds only
- Supercritical CO_2 and co-solvent extract compounds with fibers

Organic Solvent Solubility

Compounds	SB Latex (Styrene Butadiene)	PVA Latex (Polyvinyl Acetate)	Paraffin Wax (100%, no modifier)	Hot Melt Adhesive (Polyethylene-co-polyproprylene)
Organic Solvent	Toluene Swelling Chloroform Soluble	Acetone Soluble	Cyclohexane Soluble	Cyclohexane Soluble

Efficiency of Extraction

SCE \ Compounds	Styrene Butadiene	Polyvinyl Acetate	Paraffin Wax (100%, no modifier)	Hot Melt Adhesive (Polyethylene co-polypropylene)
CO_2	1%	12.5%	87.5%	25%
CO_2+ Co-solvent	12.5% Toluene	47.5% Acetone	97.5% Cyclohexane	44% Cyclohexane

Efficiency of Extraction

SCE \ Compounds	SB Latex (Styrene Butadiene)	PVA Latex (Polyvinyl Acetate)	Paraffin Wax (100%, no modifier)	Hot Melt Adhesive (Polyethylene co-polypropylene)
CO_2+ Co-solvent	12.5% pure compound Toluene	47.5% pure compound Acetone	97.5% (Cyclohexane)	44% (Cyclohexane)
Co-solvent effect	1.11	1.76	3.8	12.5
CO_2+Co-solvent+ Fibers	22.5% Latex Toluene	45% Latex Acetone	93.8% (Cyclohexane)	43% (Cyclohexane)

Conclusions

- Supercritical CO_2 with co-solvent can remove the most common stickies
- With addition of co-solvent, the extraction efficiency increases, the reaction time can be reduced to reach the same extraction ability
- Environmental perspective, selective extraction, process flexible
- Need to optimize pressure and temperature for certain compound

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Thank You!