

The use of co-solvents in supercritical debinding of ceramics

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Abstract

Extraction of organic binders (paraffin waxes) from injected green ceramic parts, by using supercritical fluids, has proven to be very efficient (short time of extraction, no defects in the green part). The extraction is more rapid when the binder is in the liquid state due to capillary migration but the capillary pressure could damage the ceramic green body because of development of internal stresses. In turn, extraction of the binder in solid state avoid formation of defects but the kinetics of extraction by solubilisation in supercritical carbon dioxide is reduced. An organic co-solvent can be added to supercritical CO₂ in order to increase the solid paraffin molecules solubility. Polar and non polar organic co-solvents were tested and their efficiency on the solubility of the paraffin molecules were compared. The influence of the length of the chains and of the number of side groups of co-solvent molecules were examined. The extraction was also performed by adding mixed co-solvent molecules. Mixtures of polar and non polar co-solvents were introduced in supercritical CO₂. Improved extraction by a factor 5 was obtained with n-hexadecane molecule as co-solvent, which represents a good compromise between destruction of the paraffin binder molecular cohesion, which requires, on one hand, large molecules, and mobility, which requires, on the other hand, small molecules. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Most of high-technology ceramics processing require the use of organic compounds (such as dispersant, binder, plasticizer) to confer suitable rheological properties and cohesion in the green state. An interesting alternative to the classical thermal debinding is the extraction of organic additives by supercritical fluids which allow, in a short time, the removal of organic additives without creation of defects in ceramic parts.^{1,2}

To remove the organic compounds, carbon dioxide is the most common solvent used in supercritical process because of its low price and of its non toxicity. Binder extraction by supercritical fluids involves different mechanisms such as solubilisation,³ diffusion^{2,4} and capillary migration (when organic compounds are in liquid state).⁴ A previous study concerned the solubility

of paraffin binders in liquid state,⁴ the solubility was experimentally measured and then computer simulated.³

Nevertheless, the main advantage of supercritical debinding is to enable the removal of the organic compounds in the solid state at low temperatures. The organic binders are, in this case, dissolved and not degraded. Then, redistribution of binder in the liquid state, inside the pores, and diffusion of degradation species, which both lead to stresses and defects in thermal debinding do not take place during supercritical debinding at low temperature. In this context, whereas the extraction rate of organic binders is higher in the liquid state, due to capillary migration and to higher solubility, supercritical extraction has to be preferably performed at low temperature for which the organic phase is solid.

In order to increase the solubility of organic solid binders in supercritical fluids, co-solvents (or entrainers) additives may be used, by analogy with the supercritical chromatography.⁵ The purpose of this paper is to present experimental results concerning the influence of some co-solvents on the solubility of a paraffin binder in supercritical conditions and to suggest some preliminary interpretations.

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2. Experimental procedure

2.1. Binder and co-solvents

A paraffin wax with a high melting temperature (73–80 °C) was used as binder in low pressure injection moulding process. Its molecular distribution was determined with the help of supercritical chromatography (Fig. 1). This paraffin is constituted of alkanes with a first peak in molecular weight population centred on the C₂₈ molecule. Carbon dioxide is supplied by Air Liquide (France). The target of this study is to determine the main directions to find an efficient co-solvent to enhance extraction of paraffin binders by supercritical CO₂. In this respect, co-solvents were chosen on the basis of two considerations: (i) polar molecules were tested because they are currently used to enhance the solubility of organic compounds in supercritical processes,^{6–8} and (ii) non polar molecules were chosen because of their positive action on the solubilization of paraffin waxes under atmospheric conditions. Organic solvents tested as co-solvents are listed in Table 1. They were used as received without preliminary purification.

The quantity of co-solvent was chosen by analogy with supercritical chromatography for which the concentration of co-solvent in supercritical carbon dioxide does not exceed 10 wt.%.⁹ For a larger amount, fluid may divide in two phases, which could be prejudicial for its efficiency. In addition, the co-solvent modifies supercritical properties and our experimental parameters (45 °C, 28 MPa) will not permit to ensure supercritical conditions of the CO₂/co-solvent mixture for a too large

amount of co-solvent. As an example (Fig. 2), an addition of 20 wt.% of ethanol in supercritical CO₂ increases the critical temperature from 31 to 75 °C and the critical pressure from 7.3 to 9.1 MPa. A concentration of co-solvent lower than 10 wt.% avoids to consider the physical aspect (supercritical properties) of the co-solvent because its concentration is not large enough to modify the supercritical properties of the fluid. Simple visual observations, using an extractor with a sapphire window, allows to evaluate the co-solvent miscibility with supercritical CO₂ and to check that the amounts of co-solvent chosen in this study (i.e. 2.5, 5 or 10 wt.%) allow to maintain one single phase in a supercritical state.

2.2. Extraction

The schematics of the equipment is described in Fig. 3.⁴ The part to be treated is submitted, in an extractor (6), to a flow of supercritical fluid (CO₂ or CO₂+co-solvent). Dissolved species are recuperated in tanks (10) in serial, maintained at different pressures.

Process temperature, regulated by heat exchanger (5) and double-wall vessel, may be adjusted from 45 to 120 °C ± 1 °C. A high-pressure membrane pump (4) can supply 1–4.5 kg/h CO₂ up to 30 MPa. Pressure is regulated with an electropneumatic valve (7) at ± 0.2 MPa. A secondary pump, usually used in high pressure liquid chromatography (HPLC), permits the introduction of the co-solvent in the process just before supercritical carbon dioxide enters the vessel. This pump can supply from 1 to 10 ml ± 1% of co-solvent per minute. Monitoring control gives the on-time evolution of the different

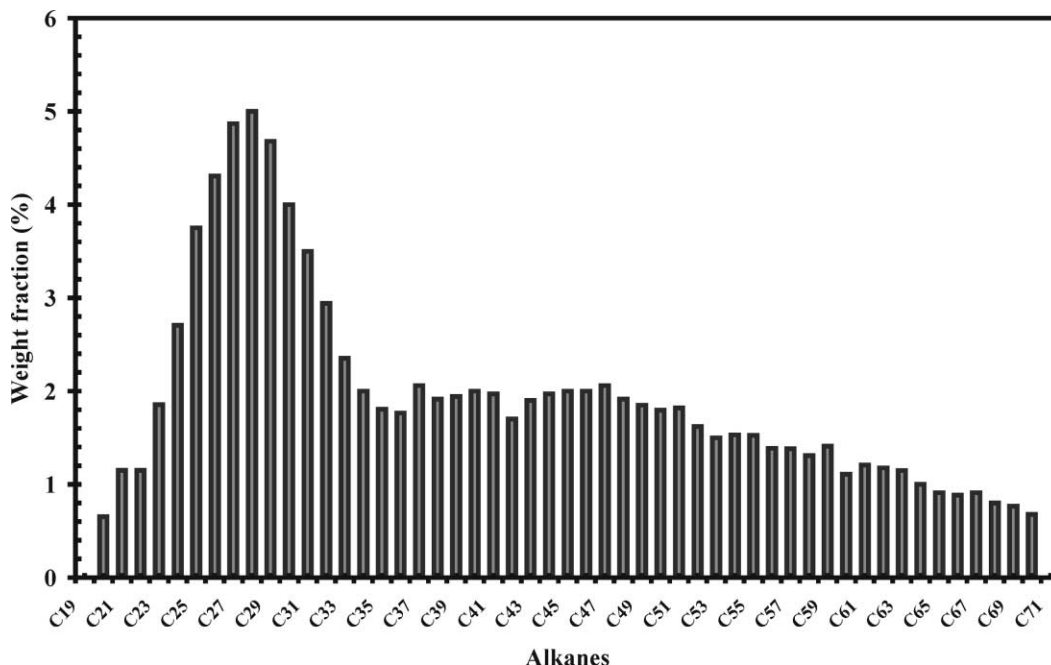


Fig. 1. Molecular distribution of the paraffin wax (m.p. = 73–80 °C).

Table 1
List of the co-solvents used and enhancement factors E obtained after 2 h of extraction

Co-solvent	Mass fraction in CO ₂	E (2 h)
<i>Polar</i>		
Ethanol (Prolabo)	2.5	1
	5–10	1.3
<i>n</i> -Butanol, <i>n</i> -hexanol (Prolabo)	2.5	1
Acetone (Prolabo)	2.5	1
	5	1.1
Tetrahydrofuran “THF” (Prolabo)	2.5	1.1
“Ether” (Prolabo)	2.5	1.2
<i>Non polar</i>		
<i>n</i> -Octane (Merck)	2.5	1
	5	1.1
<i>n</i> -Hexane, <i>n</i> -pentane (Merck)	2.5	1.1
	5	1.2
Hexadecane (Aldrich)	2.5	5
Cyclohexane (Aldrich)	2.5	1.4
Isooctane (Merck)	2.5	1.3
	5	0.9
Isopentane, isohexane (Merck)	2.5	1
	5	0.8
<i>Mixtures</i>		
2,4,4-Trimethylpentanol in ethanol (10/90) (polar) (Aldrich-Prolabo)	2.5	1.75
Petroleum ether (non polar) (Prolabo)	2.5	1
	5	1.5

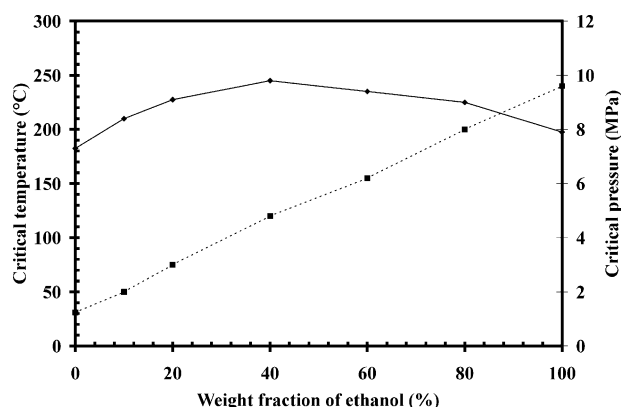


Fig. 2. Evolution of the critical temperature T_C (...) and of the critical pressure P_C (–) of CO₂ with addition of ethanol.⁵

experimental parameters (pressure, flow rate, density of supercritical CO₂, temperature, amounts of CO₂ and co-solvent injected).

Extractions were performed on cylindrical samples (20 mm diameter, 90 mm height) of moulded paraffin wax. This type of geometry permits to evaluate deformation or structural modification of the rod after extraction. Cylinders were weighted before (M_0) and after each extraction (M_t) to quantify the weight fraction (R_t) of dissolved paraffin, after a time t of extraction:

$$R_t = (M_0 - M_t)/M_0 \quad (1)$$

In order to evaluate the efficiency of the co-solvent, an enhancement factor E is calculated, after 2 h of extraction, as follow:

$$E = R_{2h}(\text{CO}_2 + \text{co-solvent})/R_{2h}(\text{CO}_2) \quad (2)$$

where $R_{2h}(\text{CO}_2 + \text{co-solvent})$ is the weight fraction of paraffin dissolved in the CO₂ containing one co-solvent after 2 h of treatment and $R_{2h}(\text{CO}_2)$ is the weight fraction of paraffin dissolved in pure supercritical CO₂ after 2 h of treatment [$R_{2h}(\text{CO}_2) = 0.033$].

3. Experimental results and discussion

Extractions were performed under a pressure of 28 MPa at 45 °C to maintain the paraffin wax in a solid state. Under these temperature and pressure conditions, solubilisation is the dominant phenomenon because of the high density of the supercritical CO₂.

3.1. Polar molecules

Polar molecules such as alcohol, ketones or ether were tested at three concentrations (2.5, 5 and 10 wt.%) in supercritical carbon dioxide. The objective was to improve interactions between the solvent (CO₂ + polar co-solvent) and the molecules of the paraffin wax. We can first suppose that polar molecules of co-solvent, with an electronic density around the oxygen atom, could induce interactions with non polar molecules of the paraffin wax. Experiments show that polar co-solvents do not significantly increase the solubility of the paraffin binder (Table 1). After 2 h of treatment, the increase of extraction is lower than 30% ($E < 1.3$). These values denote weak interactions between polar co-solvent molecules and non polar paraffin molecules. Moreover, it was established that interactions exist between the carbon atom of CO₂ molecules and the oxygen atom of polar molecules. Reilly et al.¹⁰ used a FT-IR spectroscopy to study interactions between methanol and carbon dioxide. The spectra for the combination bands denotes Lewis acid–base interactions between alcohol and carbon dioxide molecules. Gupta et al.¹¹ studied ethanol in compressed carbon dioxide. They measured a virial coefficient B , between the two previous molecules, which indicates that ethanol–gas interactions do exist. Moreover, they estimated value of K_{eq} (for the reversible one-to-one chemical interaction between CO₂ and ethanol in the gas phase) and values of standard enthalpies and entropies of association. This phenomenon may considerably decrease the effect of the supercritical fluid more than the effect of the co-solvent. Thus, polar molecules do not seem to be efficient for

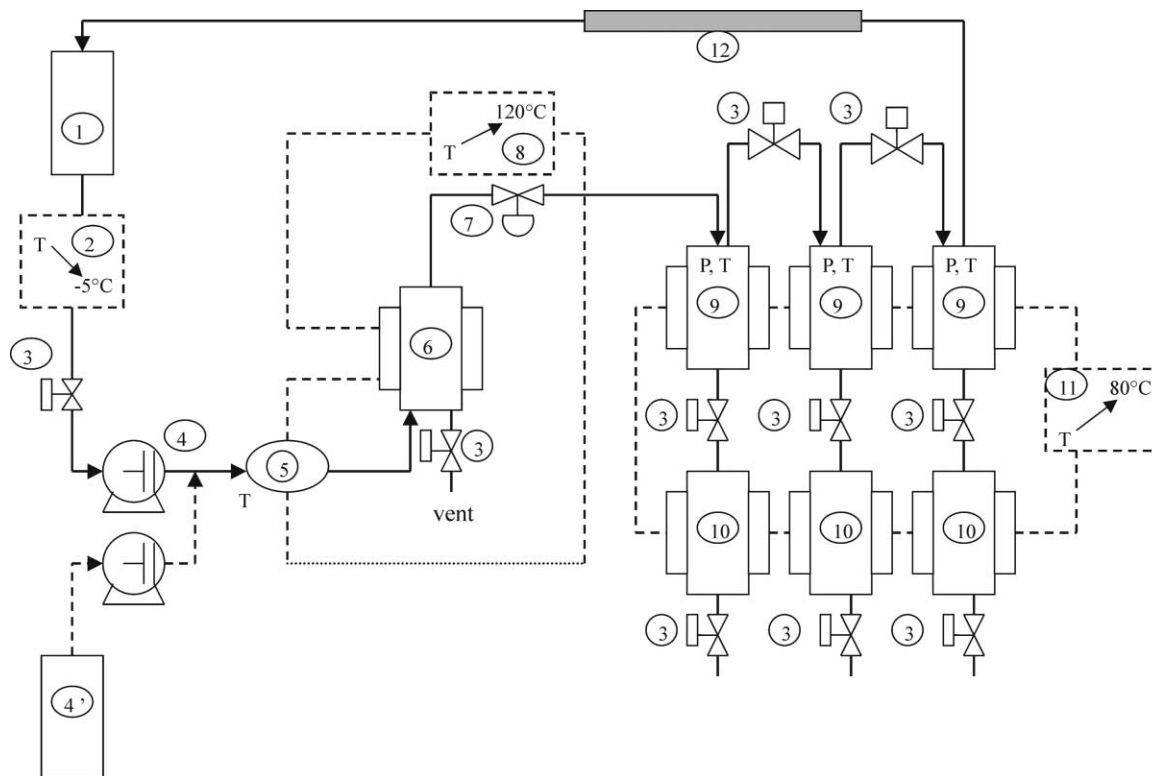


Fig. 3. Schematics of the experimental equipment: 1, CO₂ tank; 2, 8–11, heat exchangers; 3–7, automatic valves; 4, membrane pump; 5, temperature regulator; 6, double-wall vessel; 9, separator; 10, binder recuperation; 12, filter.

solubility enhancement of paraffin binder in supercritical fluids.

3.2. Non polar molecules

Electrostatic interactions such as Van der Waals interactions¹² may be improved by using co-solvent molecules which present similarity of structure and/or of composition with long alkane molecules constituting paraffin wax.¹³ In this respect, one can suppose that the extraction will be enhanced by using co-solvent molecules similar to molecules contained in the paraffin wax, because the probability of the co-solvent molecules to interact with the paraffin molecules is higher. So, non polar molecules chosen for this study will be alkanes molecules.

Homologous series of linear and branched alkanes (Table 1) were tested to know whether chain length or side groups on aliphatic chain influence solubilisation. Nevertheless, solubility could decrease with branched alkanes because of the decrease of electronic density around the co-solvent molecules.

3.2.1. Influence of the length of the co-solvent molecules

In order to study the influence of the chain length of carbon atoms, in the case of linear molecules of co-solvent, linear alkanes were studied (Table 1). The enhancement factor E varies from 1 for 2.5 wt.% of octane

($n = 8$) to 5 for 2.5 wt.% of hexadecane ($n = 16$). That suggests a significant influence on the solubility of the chain length of the co-solvent molecule. The longer the chain length of the co-solvent is, the better the extraction is. Dobbs et al.¹⁴ studied the solubility of organic non polar molecules in supercritical carbon dioxide with low amounts (3.5–7 mol%) of non polar co-solvents. They reported that the solubility increases with the size of the co-solvent molecule.

In the range of the amount of linear co-solvent introduced (0–5 wt.%), the enhancement factor increased with the co-solvent concentration. This suggests that the probability of interaction of co-solvent molecules with the linear paraffin molecules increases with the number of co-solvent molecules.

3.2.2. Influence of the number of side groups in the co-solvent molecules

The isooctane (2,2,4-methylpentane) molecule was first tested. By addition of the branched molecule isooctane in supercritical CO₂, the enhancement factor, after 2 h of treatment, increases up to a concentration of 2.5 wt.% ($E = 1.3$) then decreases for larger concentrations of co-solvent (Fig. 4). The mass fraction extracted is even lower than in pure supercritical CO₂ for isooctane addition larger than about 3.2 wt.%.

This behaviour can be explained by reference to supercritical chromatography.⁵ Above a concentration

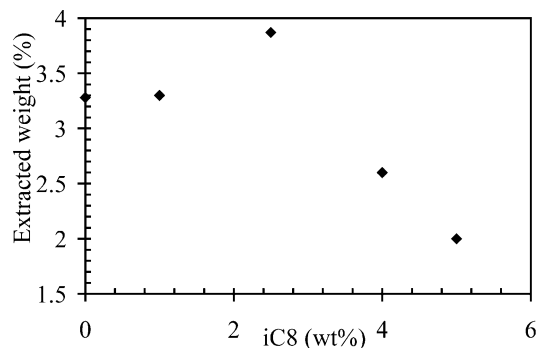


Fig. 4. Evolution of the solubility of the paraffin wax with weight fraction of isooctane in supercritical carbon dioxide (2 h—28 MPa—45 °C).

threshold of co-solvent, diffusion of the paraffin molecules is retarded by a too high concentration of co-solvent molecules which impede the mobility of the solubilized paraffin molecules. Usually, in supercritical chromatography, the threshold of co-solvent may reach 5 wt.%. In our case, non solubilised paraffin molecules contained in the rod may also contribute to a low diffusion rate of the dissolved species. The solubilisation is dominant from 0 to 2.5 wt.% of co-solvent in supercritical CO₂ (Fig. 4). Then, for higher concentrations of co-solvent, diffusion becomes the limiting step and extraction is limited by the diffusion phenomenon.

Two other branched alkanes (isopentane and isohexane) were tested to check the existence of a concentration threshold of co-solvent. After an addition of 2.5 wt.%, they do not improve the solubility (enhancement factor is equal to 1). After an increase of the concentration up to 5 wt.%, the extraction mass is decreasing by 20%.

In opposition to the behaviour of the linear co-solvent molecules, which can freely diffuse in the paraffin rod, branched co-solvent molecules are large and diffuse with difficulty. Kostov et al.¹⁵ measured the values of self-diffusion coefficient for *n*-triacontane and squalane, which is a branched isomer of the *n*-triacontane. They reported that self-diffusion coefficient of the linear molecule equals two times the self-diffusion coefficient of the branched molecule.

It is clear that the number of ramifications exercises an influence on the solubility: 2.5 wt.% isooctane (three side groups) leads to an enhancement factor equal to 1.3 whereas 2.5 wt.% of isopentane (2 methylbutane, one side group) or isohexane (2 methylpentane, one side group) does not increase extraction ($E = 1$). It is likely due to the effective volume of the branched molecule of co-solvent which is larger than those of the linear molecule of co-solvent. In order to investigate the relative influence of the effect of large molecules, we tested the cyclohexane molecule. The enhancement factor E rises to 1.4, that confirms the steric effect of large molecules of co-solvent on the solubility of paraffin molecules. Large molecules and branched molecules of co-solvent tend to

separate paraffin molecules. Solubilisation of paraffin molecules is then possible because interactions between long paraffin molecules are weakened.

4. Mixtures of co-solvents

4.1. Effect of mixture of non polar co-solvent molecules

A mixture of *n*-alkanes (C₅–C₈) and their branched isomers (i.e. petroleum ether; boiling temperature: 60–80 °C) was introduced in supercritical CO₂. Enhancement factor is comprised between 1 and 1.5 for 2.5 and 5 wt.%, respectively, of co-solvent in supercritical carbon dioxide after 2 h of treatment. Petroleum ether was tested for 3 h treatment; enhancement factor rises to 2.1. Petroleum ether molecules have a great influence on solubility of the paraffin molecules with 100% enhanced solubility.

If we consider the effect of each alkane which constitutes the petroleum ether, none has a so great influence on solubility. For instance, the enhancement factor is less than 1.5, after two hours of treatment, for *n*-pentane, *n*-octane and isooctane. A comparison between results obtained with separated alkanes and petroleum ether suggests that there is a synergy between molecules contained in petroleum ether.

4.2. Effect of mixture of polar co-solvent molecules

A solution of 2,4,4-trimethylpentanol in ethanol (10/90 vol.%) was tested as a mixture of polar co-solvents in supercritical CO₂ (2.5 wt.%). The obtained enhancement is 1.75 after 2 h of treatment. Molecules of 2,4,4-trimethylpentanol and ethanol can interact with the help of hard hydrogen atoms interactions (intermolecular hydrogen bonding: 20–40 kJ/mol¹⁶). This leads to large entities which can diffuse in the structure of the paraffin and dissociate them by decreasing their cohesion energy. The effect of this mixture seems to be only due to a physical phenomenon because no interactions between paraffin and polar co-solvent molecules exist (Section 3.1).

The action of associated co-solvent molecules on the paraffin molecules involves two mechanisms: diffusion of the associated co-solvent molecules in the paraffin and destruction of the paraffin structure. Extraction will be influenced by these two phenomenon. Nevertheless, enhanced factor obtained after 2 h treatment with the mixture 2,4,4 trimethylpentanol/ethanol is better than this obtained with the petroleum ether. This can be attributed to entities formed by association between 2,4,4-trimethylpentanol and ethanol which are larger. Entities formed by hydrogen bonds induce a larger expansion of the paraffin structure. But, one can easily imagine that associated alcohol molecules as co-solvents

will not be the ideal solution because they can rapidly become too large to diffuse easily in the paraffin structure. Moreover, they can decrease the mobility of the solubilised molecules.

Then, generally speaking, a compromise has to be found between a good diffusion favoured by small co-solvent molecules and their aptitude to destruction of the molecular cohesion of the binder favoured by large co-solvents molecules, which could be an association of molecules. In this respect, the molecule tested which constitutes a good compromise for the solubilisation of paraffin binder is the long chain ($n = 16$ which corresponds to a size of 2.3 nm), non polar, n-hexadecane molecule, which increases the extraction by a factor of 5. The petroleum ether for which molecules are associated by Van der Waals forces is less efficient with an extraction increase by a factor 1.5.

5. Conclusion

The use of co-solvents in supercritical carbon dioxide may improve the extraction of paraffin binders from a ceramic green part. Several types of interaction may take place between co-solvent molecules, binder molecules and carbon dioxide during extraction: chemical or physical interactions between paraffin molecules and co-solvent molecules which ensure enhanced solubility, Van der Waals interactions between mixed co-solvent polar molecules and interactions between polar co-solvent molecules and CO₂ molecules which decrease solubility of the paraffin. In order to characterise these interactions, we used pure paraffin. The case of extraction of ceramic body containing paraffin waxes is to consider in another part because of the influence of the body parameters (porosity) and of binder properties (viscosity,...) which could influence extractions.

More than the chemical and physical aspect of the co-solvent molecules, the mobility of the co-solvent molecules influences the solubility of the paraffin wax in the supercritical CO₂. Small molecules as linear pentane or octane have a great diffusion coefficient but they are too small to ensure chemical interactions with paraffin molecules or to destroy paraffin structure. Branched molecules ensure destruction of the paraffin rod structure but they have a low self-diffusion coefficient which leads to a threshold concentration above which the extraction rate is decreasing. In a similar way, in the case of mixtures of polar molecules, large entities formed by hard hydrogen bonds ensure the destruction of the cohesion of paraffin molecules, but threshold concentration exists.

A compromise will be found because large molecules enhance solubility but diffuse more slowly. This study leads to choose a molecule, the n-hexadecane, which

improve the solubilisation of the paraffin molecules, used as shaping binder, by a factor of 5.

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