EXTRACTION OF HO-SHO (Cinnamomum camphora Nees and Eberm Var. Linaloolifera Fujita) ESSENTIAL OIL WITH SUPERCritical CO2: EXPERIMENTS AND MODELING

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Abstract - Supercritical CO2 extraction of essential oil from the leaves of a variety of camphor tree known as Ho-Sho was studied. Experiments were carried out within the following ranges: CO2 flow rate (1 - 4 mL/min); pressure (80 - 100 bar); temperature (40 - 60 °C) and particle size (0.37 - 1.0 mm). The equipment used was an HP 8670 T extractor module with an extraction cell volume of 7 mL. Two mathematical models of the process were proposed. Model 1 was a modified version of the traditional shrinking core model with effective diffusivity and the external mass transfer coefficient as the fitting parameters. Model 2 used an additional kinetic parameter based on an Arrhenius-like expression. Both models took into account the cell pressurization step. The best fit between the extraction model curves and the experimental data was obtained using model 2.

Keywords: Supercritical extraction; Essential oil; Ho-sho; Mathematical modeling.

INTRODUCTION

Linalool is an important intermediary in the manufacture of vitamin E and, like geranial, is raw material for the production of vitamin A (Bauer and Garbe, 1985). Linalool can be synthesized by different chemical routes from α-pinene or from isoprene. The world consumption of linalool in 1988 was estimated at six million metric tons (Clark, 1988) and it is growing year after year, because it is used not only for the production of vitamins, but also in the fragrance industry. An alternative for the production of linalool from a natural source is the essential oil obtained from a plant known as ho-sho (Cinnamomum camphora Nees and Eberm var. linaloolifera Fujita), which is a tree native to China, Formosa and Japan. The main component of ho-sho essential oil is linalool (80-90%). Natural sources of linalool are of interest, mainly to the fragrance industry, because the smell of plant materials is usually the result of complex interactions among the components of the mixture (Reverchon, 1997).

In this work we studied the extraction of ho-sho essential oil using supercritical CO2 as solvent, because this process produces oils of excellent quality and also is an example of clean technology.

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MATERIALS AND METHODS

Ho-sho leaves from exemplars of plants at the Biotechnology Institute of the University of Caxias do Sul were picked and dried under controlled conditions (temperature 20-22 °C and relative air humidity 50-60%) during a period of seven days. After the drying period the leaves were ground using a Tecnal TE-650 mill (Tecnal, Brazil). Tyler sieves were used to classify particles by desired size fractions (average diameters of 0.37 mm, 0.50 mm and 1.0 mm). Then the particles were introduced into the extraction cell, whose internal volume was about 7 mL.

The experimental extraction runs with supercritical CO2 were carried out in a Hewlett-Packard 7680 T extraction module and followed a 3x3 graeco-latin square design type, according to the experimental matrix presented in Table 1:

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow Rate (mL/min)</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Particle Size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>80</td>
<td>40</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>90</td>
<td>50</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>100</td>
<td>60</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>80</td>
<td>50</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>90</td>
<td>60</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>100</td>
<td>40</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>80</td>
<td>60</td>
<td>1.00</td>
</tr>
<tr>
<td>8</td>
<td>4.0</td>
<td>90</td>
<td>40</td>
<td>1.00</td>
</tr>
<tr>
<td>9</td>
<td>4.0</td>
<td>100</td>
<td>50</td>
<td>0.37</td>
</tr>
</tbody>
</table>

For each run, the oil obtained at predefined time intervals was collected in separate flasks and the data points were used to plot the extraction curves.

Gas chromatography using an internal standard was the method used for quantification of the essential oil extracted. This method consists in adding a given amount of a substance (which is called the standard) to the extract before the chromatographic analysis. This substance must have a response factor similar to that of the main components of the extract. In accordance with this criterion, 3-octanol (Aldrich, USA, 97% purity) was chosen as internal standard for having a molar mass close to that of linalool, the main component in the extracted essential oil. It was also assumed that the other oil components had the same response factor. Thus, the total amount of essential oil extracted was calculated using the results of the chromatographic analysis and the extract yield was determined. All the analyses were carried out in a gas chromatograph HP GC 6890 Series, equipped with a data acquisition software (HP Chemstation), an FID detector (Flame Ionization Detector) and a fused silica capillary column HP-Innowax (30 m x 320 μm). The column temperature varied from 40 °C (8 minutes) to 180 °C at 3 °C/min, from 180 to 230°C at 20 °C/min, 230 °C (20 minutes). The injector temperature was 250 °C; the split ratio was 1:50; H2 was the carrier gas; the column head pressure was 34 kPa and the injected sample volume was 1.0 μL.

The density of the porous solid matrix and the tortuosity of the solid were determined with a mercury intrusion assay using Poresizer 9320 equipment (Micromeritics, USA), obtaining the values of 544.5 kg/m³ and 6.71, respectively. The skeletal density of the solid was determined using a helium pycnometer (Ultrapycnometer 1000, Quantachrome, USA), and the value obtained was 1314 kg/m³. From the density of the porous solid and the skeletal density it was possible to determine the porosity of the solids as being 0.58.

MATHEMATICAL MODELING

The proposal presented in this work includes the mathematical modeling of the extractor pressurization stage, besides the extraction stage itself. Thus, the initial conditions for the extraction stage will be the ones obtained by the end of the pressurization stage. In the pressurization stage, the fluid phase is modeled as an infinite bath. The fluid properties are assumed to be dependent only on time. For each experiment, the variation in pressure with time was measured and then fitted by an algebraic expression. Extractor pressurization was conducted isothermally. CO2 density was estimated using the Peng-Robinson equation of state. Therefore, the equation for the fluid phase in the pressurization stage can be written as
\[
\frac{dC_1(t)}{dt} = \frac{C_1(t)}{\rho_1(t)} \frac{dp_1(t)}{dt} - \frac{(1 - \varepsilon) 3k_{f1}(t)}{\varepsilon R} \left( C_1(t) - C_{p1}(r, t) \bigg|_{r=R} \right)
\]

where \(C_1\) is the solute concentration in CO\(_2\) in the bed void volume, \(\rho_1\) is the density of CO\(_2\), \(\varepsilon\) is the voidage of the extraction bed, \(k_{f1}\) is the external film mass transfer coefficient, \(R\) is the particle radius, \(C_{p1}\bigg|_{r=R}\) is the solute concentration in the pore volume of solid at the surface of the particle and \(t\) is time.

Initial condition:
\[C_1(0) = 0\]  

For the extraction stage, the fluid phase equation is obtained assuming the axial dispersion term and the process occurring under isothermal and isobaric conditions. The resulting equation is
\[
\frac{\partial C(z, t)}{\partial t} = D_L \frac{\partial^2 C(z, t)}{\partial z^2} - \nu \frac{\partial C(z, t)}{\partial z} - \frac{(1 - \varepsilon) 3k_{f1}}{\varepsilon R} \left( C(z, t) - C_{p1}(z, r, t) \bigg|_{r=R} \right)
\]

where \(C\) is the solute concentration in CO\(_2\) in the bed void volume in the extraction stage, \(D_L\) is the axial dispersion coefficient, \(\nu\) is the interstitial velocity of solvent in the bed, \(k_{f1}\) is the external film mass transfer coefficient in the extraction stage, \(C_{p1}\bigg|_{r=R}\) is the solute concentration in the pore volume of solid at the surface of the particle in the extraction stage and \(z\) is the axial coordinate.

Initial condition:
\[C(z, 0) = C_1(t = \text{pressurization time}) \forall z\]  

Boundary conditions:
\[z = 0, \quad \nu C(z, t) - D_L \frac{\partial C(z, t)}{\partial z} = 0 \forall t\]  
\[z = L, \quad \frac{\partial C(z, t)}{\partial z} = 0 \forall t\]

Pressurization stage:
\[
\frac{\partial C_{p1}(r, t)}{\partial t} = \frac{D_{ef1}(t)}{\varepsilon_p} \left( \frac{\partial^2 C_{p1}(r, t)}{\partial r^2} + \frac{2 \partial C_{p1}(r, t)}{r \partial r} \right) - \frac{C_{p1}(r, t) dp_1(t)}{\rho_1(t)} \frac{dt}{dt}
\]

where \(D_{ef1}\) is the effective diffusivity in the extractor pressurization stage, \(\varepsilon_p\) is the porosity of the solid and \(r\) is the radial coordinate.

Initial condition:
\[C_{p1}(r, 0) = 0 \forall r\]

Boundary conditions:
\[r = r_c; \quad C_{p1}(r, t) = C_{sat1}(t)\]
if \(r_c \neq 0\)
\[r = r_{c1}; \quad \frac{\partial C_{p1}(r, t)}{\partial r} = 0 \text{ (symmetry)}\]  
if \(r_{c1} = 0\)

For the mass balance in the solid phase, two distinct models based on differential method of rate analysis are proposed. Model 1 is based on the shrinking core model, traditionally used in the chemical reactor area, where it is known as the “non-reacted core model”; initially adapted by Roy et al. (1996) and improved by Spricigo (1998). The model assumes the existence of a solute core inside a spherical particle that will decrease continuously during extraction. The equation that governs mass transfer inside the particle pores assumes an effective diffusivity for the oil in the CO\(_2\). The solute diffuses inside the pores in the region between core surface \((r = r_c)\) and particle surface \((r = R)\). It is assumed that, on the core surface, the solvent is always saturated. The solubility of the essential oil was calculated from the results of Chang and Chen (1999), assuming the oil to be pure linalool. When the core vanishes, the boundary condition for the pore oil concentration becomes a symmetry condition. Thus, the model obtained for the solid phase can be written as

Initial condition:
\[C_{p1}(0, r) = 0 \forall r\]

Boundary conditions:
\[r = r_c; \quad C_{p1}(r, t) = C_{sat1}(t)\]
if \(r_c \neq 0\)
\[r = r_{c1}; \quad \frac{\partial C_{p1}(r, t)}{\partial r} = 0 \text{ (symmetry)}\]  
if \(r_{c1} = 0\)
where \( D_{ef} \) is the effective diffusivity in the extraction stage and \( C_p \) is the solute concentration in the pore volume of solid in the extraction stage.

**Initial condition:**

\[
P_{1}(z,r,0) = C_{p_{1}}(r,t = \text{pressurization time}) \quad (\forall z) \quad (13)
\]

**Boundary conditions:**

\[
r = r_c; \quad \frac{\partial C_p(z,r,t)}{\partial r} = 0 \quad \text{(symmetry)} \quad \text{if} \quad r_c = 0 \quad (15)
\]

\[
r = R; \quad \frac{\partial C_p(z,r,t)}{\partial r} \bigg|_{r=R} = k_f \left( C(z,t) - C_{p_{1}}(z,r,t) \right) \quad (\forall t) \quad (16)
\]

The present proposal for calculation of the shrinkage of the core differs from that of Spricigo (1998). In this work it is assumed that the variation in oil mass in the core is equal to the oil mass flow rate at the surface of core multiplied by the surface area of the core. After the algebraic calculation the equations obtained for both stages of the process become

**Pressurization stage:**

\[
\frac{dC_{p_{1}}(r,t)}{dt} = \frac{D_{ef}(t)}{C_N} \cdot \frac{\rho_s}{\rho_{s_{1}}(t)} \cdot \frac{\partial C_{p_{1}}(r,t)}{\partial r} \bigg|_{r=r_{c_{1}}} \quad (17)
\]

**Initial condition:**

\[
r_{c_{1}}(t = \text{pressurization time}) = R \quad (18)
\]

**Extraction stage:**

\[
\frac{\partial C_p(z,r,t)}{\partial t} = \frac{D_{ef}}{C_N} \cdot \frac{\rho_s}{\rho_s} \cdot \frac{\partial C_p(z,r,t)}{\partial r} \quad (r = r_c) \quad (19)
\]

where \( \rho \) is the density of \( \text{CO}_2 \) in the extraction stage.

**Initial condition:**

\[
r_c(z,0) = r_{c_{1}}(t = \text{pressurization time}) \quad (\forall z) \quad (20)
\]

Model 2 makes use of a differential equation for diffusion inside the pores that is applied to the whole particle domain (different from model 1 where diffusion takes place outside the core region) and an equation for mass transfer from solid to fluid based on oil solid concentration and the distance from saturation in the fluid phase. A radial gradient of solid oil concentration, instead of an average concentration value as is usually seen in the literature was assumed. Therefore, the equations for the solid phase in model 2 are

**Pressurization stage:**

\[
\frac{\partial C_{p_{1}}(r,t)}{\partial t} = \frac{D_{ef}(t)}{C_N} \cdot \frac{\rho_s}{\rho_{s_{1}}(t)} \cdot \frac{\partial C_{p_{1}}(r,t)}{\partial r} - \frac{C_{p_{1}}(r,t) \cdot \rho_{s_{1}}(t)}{\rho_s(t)} \cdot \frac{\partial q_{s_{1}}(r,t)}{\partial t} - K(T) \cdot \rho_s(t) \quad (19)
\]

\[
q_{s_{1}}(r,t) \left( C_{sat}(t) - C_{p_{1}}(r,t) \right) \quad (22)
\]

where \( q_s \) is the solute concentration in the solid phase in the extractor pressurization stage and \( K \) is a kinetic parameter.

**Initial conditions:**

\[
P_{1}(r,0) = 0 \quad (\forall r) \quad (23)
\]

\[
q_s(r,0) = C_N \quad (\forall r) \quad (24)
\]
Boundary conditions:
\[ r = 0; \quad \frac{\partial C_{pl}(r,t)}{\partial r} = 0 \quad \text{(symmetry)} \quad (25) \]
\[ r = R; \]
\[ D_{ef}(t) \frac{\partial C_{pl}(r,t)}{\partial r} \bigg|_{r=R} = k_f(t) \left( C_{i}(t) - C_{pl}(r,t) \right) \quad (\forall t) \quad (26) \]

Extraction stage:
\[ \frac{\partial C_p(z,r,t)}{\partial t} = \frac{D_{ef}}{\varepsilon_p} \left( \frac{\partial^2 C_p(z,r,t)}{\partial z^2} + \frac{2}{r} \frac{\partial C_p(z,r,t)}{\partial r} \right) - \frac{\rho_s}{\varepsilon_p} \frac{\partial q(z,r,t)}{\partial t} \quad (27) \]
\[ \frac{\partial q(z,r,t)}{\partial t} = -K(T) \rho q(z,r,t) \left( C_{sat} - C_p(z,r,t) \right) \quad (28) \]
where \( q \) is the solute concentration in the solid phase in the extraction stage.

Initial conditions:
\[ C_p(z,r,0) = C_{pl}(r,t = \text{pressurization time}) \quad (\forall z) \quad (29) \]
\[ q(z,r,0) = q_i(r,t = \text{pressurization time}) \quad (\forall z) \quad (30) \]

Boundary conditions:
\[ r = 0; \quad \frac{\partial C_p(z,r,t)}{\partial r} = 0 \quad \text{(symmetry)} \quad (31) \]
\[ r = R \]
\[ D_{ef} \frac{\partial C_p(z,r,t)}{\partial r} \bigg|_{r=R} = k_f \left( C(z,t) - C_p(z,r,t) \right) \quad (\forall t). \quad (32) \]

The axial dispersion coefficient was estimated by a correlation proposed by Tan and Liou (1989). The models were solved by the method of lines, through spatial discretization using finite differences followed by an integration in time using Euler’s method.

RESULTS AND DISCUSSION

In the simulations performed, the external film mass transfer coefficient \( (k_f) \), the effective diffusivity \( (D_{ef}) \) and, in case of model 2, the kinetic coefficient \( (K) \) were used as the fitting parameters. The initial estimates for the external film mass transfer coefficient were obtained by Wakao and Kagumi’s (1982) correlation. For the effective diffusivity the starting value was obtained with the equation proposed by Pinto (1994). The initial estimates for the kinetic parameter \( (K) \) were obtained as a function of temperature, using an Arrhenius-like expression.

The parameters were optimized without using a specific algorithm, i.e., by a process of trial and error, by minimizing an objective function \( (F) \), defined by
\[ F = \sum_{i}^{n} (M_{\text{calc},i} - M_{\text{exp},i})^2 \quad (33) \]
where \( n \) is the number of experimental points for each run, \( M_{\text{calc},i} \) is the accumulated extracted oil mass up to the time corresponding to point \( i \), obtained by simulation and \( M_{\text{exp},i} \) is the accumulated oil mass extracted up to the time corresponding to point \( i \), obtained experimentally.

During the optimization process, in both models a low sensitivity to the external film mass transfer coefficient was verified, indicating that extraction is controlled by intraparticle mass transfer. Thus, the option was to keep the values of these parameters obtained directly by Wakao and Kagumi’s (1982) correlation. Related to the effective diffusivity parameter, the final values obtained for each experiment were from one to two orders of magnitude smaller than the initial estimates. The difficulty faced in this parameter prediction is associated with the fact that different vegetal structure types have different mass transfer resistances, which makes it more difficult to correlate the effective diffusivity with the oil-CO₂ binary diffusivity, as reported by Gaspar et al. (2003).

The initial guess for the kinetic parameter \( (K) \), obtained with an Arrhenius-like equation, using a value for the frequency factor of \( 1.0 \times 10^{13} \text{ m}^2\text{kg}^{-1}\text{s}^{-1} \) and an activation energy of \( 1.0 \times 10^5 \text{ J/mol} \), resulted in values from one to two orders of magnitude smaller than the values obtained at the end of optimization. As the value for the frequency factor was somewhat arbitrary, a correction of this factor could be incorporated, allowing better initial estimates. The results obtained in the optimization are reported in Table 2:
The extraction curves for run 2 are shown in Figure 1, where the results for both models were obtained with the optimized parameters. In general, the best agreement between the experimental data and the calculated values was obtained with model 2.

Figures 2 and 3 show respectively the concentration profiles in the pores of the particles at the inlet of the extractor (z = 0) for run 4 in model 1 and model 2. In Figure 2, a change in the curves due to the gradual reduction of the core can be noted.

The variation in core size (Model 1) with time and axial position in the extractor for run 4 is shown in Figure 4. It includes the pressurization stage besides the extraction stage. The depletion of oil in the particles begins at the inlet of the extractor, where the solid is in contact with pure CO\textsubscript{2} and extends in the direction of the outlet.

### Table 2: Values of optimized model parameters

<table>
<thead>
<tr>
<th>Run</th>
<th>( k_f \times 10^4 ) (m/s)</th>
<th>( D_f (\text{m}^2/\text{s}) ) Model 1</th>
<th>( D_f (\text{m}^2/\text{s}) ) Model 2</th>
<th>( K (\text{m}^3/\text{kg} \cdot \text{s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.351</td>
<td>4.105 x 10\textsuperscript{12}</td>
<td>2.085 x 10\textsuperscript{-11}</td>
<td>2.047 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>2</td>
<td>2.525</td>
<td>8.537 x 10\textsuperscript{12}</td>
<td>3.309 x 10\textsuperscript{-11}</td>
<td>2.489 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>3</td>
<td>1.513</td>
<td>7.834 x 10\textsuperscript{11}</td>
<td>7.700 x 10\textsuperscript{-11}</td>
<td>1.340 x 10\textsuperscript{-1}</td>
</tr>
<tr>
<td>4</td>
<td>2.316</td>
<td>4.631 x 10\textsuperscript{11}</td>
<td>4.308 x 10\textsuperscript{-11}</td>
<td>6.728 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>5</td>
<td>4.895</td>
<td>4.024 x 10\textsuperscript{11}</td>
<td>6.163 x 10\textsuperscript{-11}</td>
<td>2.058 x 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>6</td>
<td>2.302</td>
<td>7.146 x 10\textsuperscript{12}</td>
<td>5.287 x 10\textsuperscript{-12}</td>
<td>6.141 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>7</td>
<td>4.991</td>
<td>9.717 x 10\textsuperscript{11}</td>
<td>1.580 x 10\textsuperscript{-10}</td>
<td>3.087 x 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>8</td>
<td>2.182</td>
<td>2.127 x 10\textsuperscript{11}</td>
<td>1.634 x 10\textsuperscript{-11}</td>
<td>1.433 x 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>9</td>
<td>5.406</td>
<td>2.269 x 10\textsuperscript{11}</td>
<td>1.771 x 10\textsuperscript{-11}</td>
<td>3.700 x 10\textsuperscript{-2}</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this work, two mathematical models were proposed to represent the process of supercritical extraction of essential oil from leaves of a plant known as ho-sho, using CO₂ as solvent. Both models contemplated the initial stage of extractor pressurization, which differentiates this work from previous research found in the literature. This can be important in the scale-up of the process, depending on the volume of the extractor and the capacity of the pump. The model that best reproduced the extraction curves was model 2, which used a nonconventional kinetic parameter based on an Arrhenius-like equation. It was found that extraction is controlled by intraparticle mass transfer. Additional work has to be done for correlate the effective diffusivity with the oil-CO₂ binary diffusivity. For the set of experiments performed, the largest essential oil yield obtained (4.31% w/w dry weight basis) occurred under the following conditions: a pressure of 90 bar, a temperature of 60 °C, a CO₂ flow rate of 2.5 mL/min and a particle size of 0.37 mm.

NOMENCLATURE

Latin Letters

\[ C_1(t) \] solute concentration in CO₂ in the bed void volume in the extractor

\[ C(z, t) \] solute concentration in CO₂ in the bed void volume in the extraction stage

\[ C_N \] initial solid phase concentration

\[ p_1C(r, t) \] solute concentration in the pores of the solid in the extractor pressurization stage

\[ pC(z, r, t) \] solute concentration in the pores of the solid in the extraction stage

\[ sat_1C(t) \] saturation concentration of solute in the fluid phase in the extractor pressurization stage

\[ satC \] saturation concentration of solute in the fluid phase

\[ ef_1D(t) \] effective diffusivity in the extractor pressurization stage

\[ efD \] effective diffusivity in the extraction stage

\[ LD \] axial dispersion coefficient

\[ k_f(t) \] external film mass transfer coefficient in the
extractor pressurization stage

\( k_f \) external film mass transfer coefficient in the extraction stage (m/s)

\( K \) kinetic parameter \( (m^3 \text{ kg}^{-1} \text{s}^{-1}) \)

\( L \) bed length (m)

\( q_i(r,t) \) solute concentration in the solid phase in the extractor pressurization stage (kg oil/kg solid)

\( q(z,r,t) \) solute concentration in the solid phase in the extraction stage (kg oil/kg solid)

\( r \) radial coordinate in the particle (m)

\( r_c(t) \) core radius in the extractor pressurization stage (m)

\( r_c(z,t) \) core radius in the extraction stage (m)

\( R \) particle radius (m)

\( t \) time (s)

\( T \) temperature (K)

\( z \) axial coordinate (m)

**Greek Letters**

\( \varepsilon \) voidage of the extraction bed (dimensionless)

\( \varepsilon_p \) porosity of the solid (dimensionless)

\( \nu \) interstitial velocity of solvent in the bed (m/s)

\( \rho_l(t) \) density of CO\(_2\) in the extractor pressurization stage (kg/m\(^3\))

\( \rho \) density of CO\(_2\) in the extraction stage (kg/m\(^3\))

\( \rho_s \) density of the porous solid matrix (kg/m\(^3\))

**REFERENCES**


