Drying and Impregnation of Wood with Propiconazole Using Supercritical Carbon Dioxide

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Abstract—The process of wood drying is studied in supercritical (SC) CO_2 and SC-CO_2 containing 5 vol % ethanol at temperatures of 323, 343, and 353 K and pressures of 10, 20, and 30 MPa. It is established that 40–87% of moisture is removed from wood in the first cycle of drying. An increase in the duration of the decompression stage of the drying process decreases the number of cracks in the wood samples. The solubility of propiconazole is studied in SC-CO_2 at 323, 343, and 353 K in the pressure range of 10–30 MPa using a dynamic method. Rather high saturation concentrations of $(3-5) \times 10^{-3}$ mol/mol CO_2 are obtained, which indicates the potential benefits of using SC-CO_2 as a solvent in wood impregnation with propiconazole. Continuous impregnation is achieved when impregnating wood with propiconazole from SC-CO_2. The impregnation efficiency increases with increasing pressure and duration of the process.

Keywords: propiconazole, supercritical CO_2, solubility, wood, drying, impregnation
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INTRODUCTION

Wood is an important and valuable raw material. It is widely used in many branches of industry and construction in the form of lumber, railway sleepers, pillars, etc. Wood has a number of valuable properties, including excellent external characteristics, strength, hardness, and environmental friendliness. However, wood, unless treated with protective agents, is susceptible to rather rapid destruction. The processes of wood destruction (decay) can be prevented by impregnation with antiseptics. Traditional methods of so-called liquid impregnation [1–3] are ineffective and do not provide continuous impregnation of wood; their industrial application is therefore limited. One way to address these problems is to use supercritical fluid (SCF) impregnation [4, 5], the appeal of which is primarily determined by the high penetrating ability of supercritical solvents, which enables the continuous impregnation of wood. This technological approach has been developed over the past 15–20 years.

Not all issues have been resolved, however: the search for advantageous (and ecologically safe) impregnating compounds continues and the stage of preliminary drying of wood is being improved.

It is known that excessive pressure gradients in wood and high rates of their change often lead to the destruction of the wood structure. To date, there are relatively few studies on the effect of SCF impregnation on the physical and mechanical properties of wood [6–12] and these works are mainly devoted to the study of the process parameters on the strength of different wood samples. The available results can be characterized as ambiguous. For instance, although no significant effect of impregnation on the Young's modulus and the modulus of elasticity was established in [6, 7], a significant decrease in the strength of southern pine wood samples was observed in [8]. In [9, 10], the effect that the pressure maintained during the impregnation process had on the Young's modulus and the modulus of elasticity of different types of wood turned out to be substantially unequal. For some types of woods, the process parameters had no significant effect on the strength characteristics, but for other woods, they led to a significant decrease in these characteristics.

The kinetics of impregnation and the way it is affected by the process parameters have been discussed in more detail in the literature. For example, it is mentioned in [11] that pressure has a greater effect on the amount of substance introduced into wood than the duration of the impregnation process.

The Superwood[TM] technology (developed by Hampen, Denmark) deserves special attention [13]. It involves a complex treatment of wood with a multicomponent impregnating solution based on SC-CO_2 to provide a number of important properties to the wood (incombustibility and resistance to various bio-

logical and atmospheric factors) and to simultaneously stain it. According to the company, this technology has been commercialized but its further commercial history is unknown. Moreover, important information on the physicochemical basis of this technology is unavailable, which makes it impossible to draw unambiguous conclusions on its technical maturity or the quality of the impregnating compositions and selected regimes at the stages of the preliminary preparation of the material and its impregnation.

When implementing SCF technology, the optimization of the composition of the impregnating solution requires data on the solubility of the impregnating substance in the SCF solvent. These data make it possible to establish the possibility of the impregnation process and its optimum parameters.

In almost all woodworking applications, the impregnation process is preceded by the process of wood drying. Traditional wood drying methods are energy-intensive and time-consuming [14]. In the present study, we use the SC-CO$_2$ extraction process as an alternative to the traditional methods.

Therefore, the aim of this work is to study:

(1) the solubility of the impregnating material (propiconazole) in the SCF solvent;

(2) the possibility of wood drying in the SC-CO$_2$-based extraction process; and

(3) the impregnation of wood samples using SC-CO$_2$.

Fungicide propiconazole was selected as a model substance. Its chemical formula is $C_{15}H_{17}Cl_2N_3O_2$; its IUPAC name is (+/−)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-methyl]-1H-1,2,4-triazole.

EXPERIMENTAL

Propiconazole (99% purity; Hefei TNJ Chemical Industry Co.), which is a viscous yellow liquid, was chosen as the active agent of the impregnating composition. The isomeric composition and purity of the propiconazole were studied by chromatography—mass spectrometry on a DFS device (Thermo Electron Corporation, Germany). The ionization method was electron impact; the energy of the ionizing electrons was 70 eV; the temperature of the ion source was 523 K. We used an ID-BP5X capillary column (which is an analog of DB-5MS) from SGE (Scientific Glass Engineering, Australia). Its length was 50 m; its diameter was 0.32 mm; the chemical composition of the phase was 5% diphenyl and 95% dimethylpolysiloxane; and the phase layer thickness was 0.25 μm. The carrier gas was helium. Mass spectral data were processed using the Xcalibur software. A test sample was diluted in chromatographically pure acetone to the concentration of 5 vol % before being introduced into the device.

The chromatographic analysis shows that the test substance is virtually free from impurities (not less than 99% pure) and that it is a mixture of cis- and trans-isomers of propiconazole.

Figure 1 shows a schematic diagram of the experimental setup for the solubility determination by a dynamic method.

The setup comprises systems for the pressure generation and maintenance and temperature generation and maintenance, as well as a high-pressure extractor. The pressure-generation system comprises CO$_2$ cylinder 1, Supercritical 24 pump 2 (Thar Technology), and BP66-1A11SJ0151 pressure regulator 3 (Go-Reg). The accuracy of maintaining the pressure is ±0.03 MPa. Pressure control is carried out using a standard manometer of the 0.15 accuracy class. The device makes it possible to study the solubility of substances in carbon dioxide in the temperature range of 273—450 K at pressures of up to 30 MPa. The temperature control system makes it possible to maintain preset temperatures with an accuracy of ±0.25°C.

The flow rate of CO$_2$ is set with an accuracy of ±5% using a pump. The amount of gas that is passed through the measuring cell during one measurement is defined by the difference in the weights indicated by an AnD GP100K scale of a high accuracy class (II) before and after the experiment.

The main part of the experimental setup is tubular extractor 3 made of stainless steel; its height is 2 m and its inside diameter is 10 mm. Meshes with micron-sized cells are installed at the column entrance and exit to improve the flow distribution over the cross section of the column. To intensify the heat- and mass-transfer processes, the column is filled with rings from Inzhekhim 2000.

After a sample of the test substance (propiconazole) is placed into the extraction cell, the heat is turned on, carbon dioxide is supplied, and predetermined pressure and temperature values are set. The flow rate of the gas that passes through the extractor is regulated by the pressure regulator. After passing through the pressure regulator, the substance dissolved in SC-CO$_2$ enters trap 11. After the experiment, the studied material is extracted from the trap and weighed on a Vibra analytical scale 10 with an accuracy of 0.0001 g. The solubility of propiconazole in SC-CO$_2$ is calculated based on this mass and the respective amount of carbon dioxide.

To verify the reliability of the results of these studies, we performed control measurements of the solubility of n-hexadecane (cetane) in SC-CO$_2$ (Fig. 2), for which there are reliable experimental data [15].

The results of the present study agree with the literature data within the total measurement error; the deviation does not exceed 4.3%.

The second experimental setup presented in Fig. 3 was designed based on a SFE-1000 SCF extraction system (Waters, USA) and used to study the wood drying process.
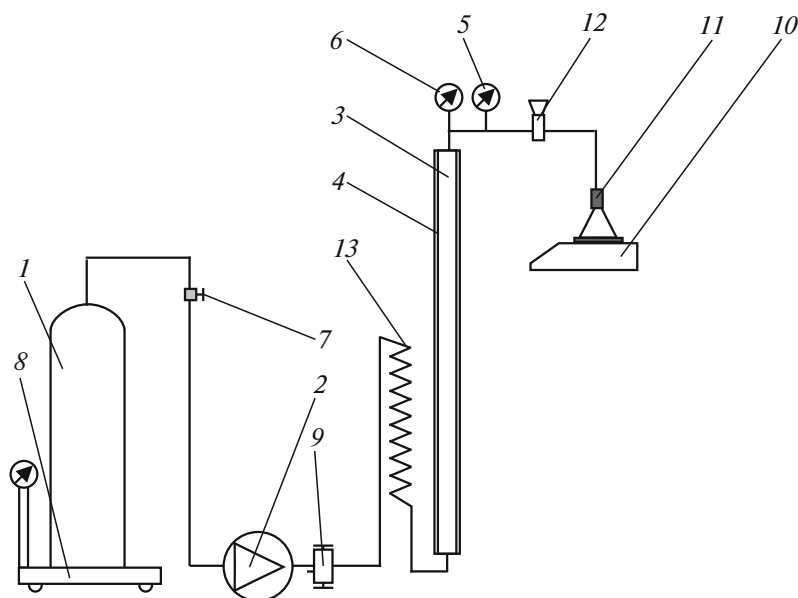
Fig. 1. Scheme of the experimental setup: *1*—CO$_2$ cylinder; *2*—pump; *3*—extractor; *4*—extractor heater; *5* and *6*—pressure and temperature sensors; *7* and *9*—shut-off and regulating valves; *8* and *10*—scales; *11*—trap; *12*—back pressure regulator; and *13*—preliminary heating of CO$_2$.
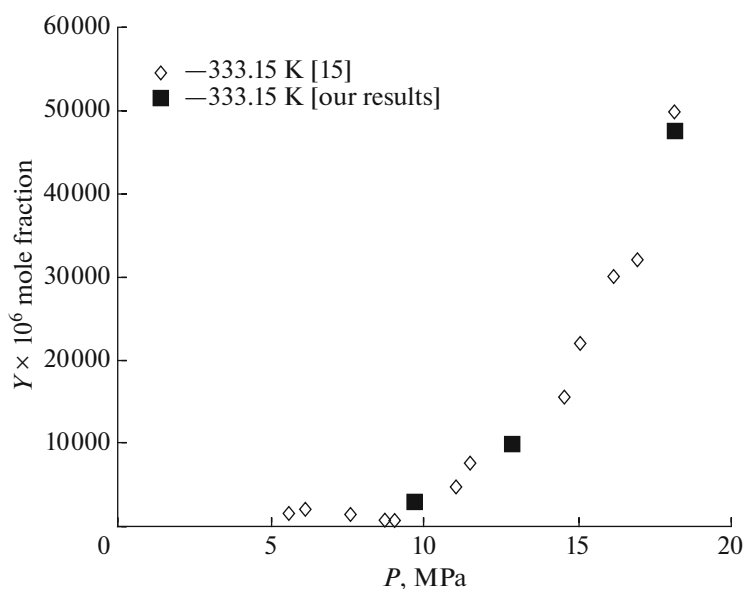

Fig. 2. Solubility of n-hexadecane (cetane) in SC-CO$_2$ at 333 K.

The pressure generation system consists of a 50-L CO$_2$ cylinder *1* and refrigeration unit *2*, which cools the working chambers of plunger gradient pump *3* (Thar Technology, USA). At the start of the experiments, CO$_2$ is cooled and condensed in the working chamber of the pump by the refrigeration unit. The pump plunger pushes liquid CO$_2$ out into the system. The operating pressure in the system is measured by digital manometer *10*. The gas flow rate is set by a Coriolis mass flowmeter. Data are displayed on a control system display or a computer via an RS 232C interface.

The carbon dioxide that enters drying chamber *7* is heated by electric heater *6*.

Pine with an initial moisture content of 60–89% was chosen as the wood species of the study. Some samples with the maximum moisture content were preconditioned in water in water for one month. The moisture content of each sample before and after the drying process was determined by the weight method in accordance with *GOST 16483.7-71*.
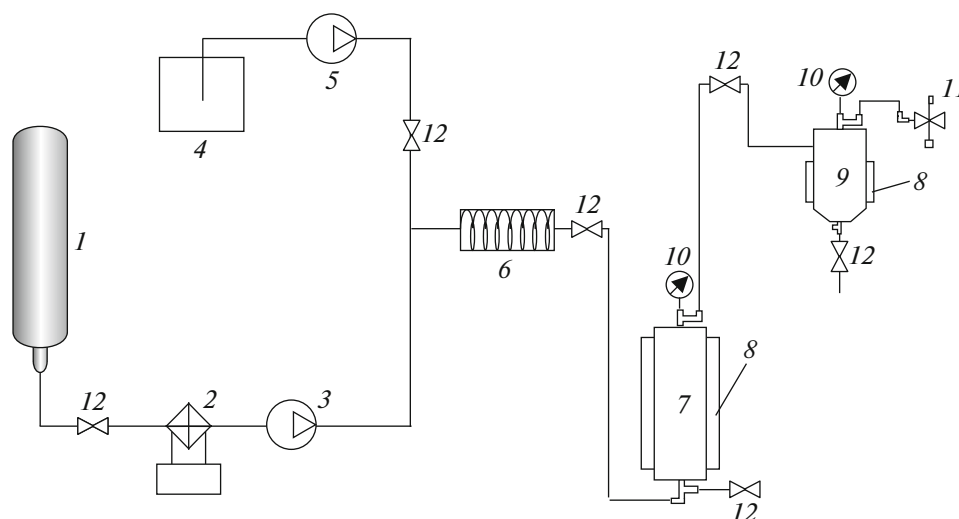
Fig. 3. Scheme of the experimental setup for drying wood in SC-CO$_2$: *1*—CO$_2$ cylinder; *2*—refrigerator; *3*—CO$_2$ pump; *4*—cosolvent tank; *5*—cosolvent pump; *6*—electric heater; *7*—drying chamber; *8*—heating jacket; *9*—cyclone separator; *10*—manometer; *11*—manual needle valve; *12*—high pressure valves.

In this study, wood samples were subjected to the extraction drying with SC-CO$_2$ (pure SC-CO$_2$ and SC-CO$_2$ modified by the addition of 5% ethanol) at temperatures of 323, 343, and 353 K; pressures of 10, 20, and 30 MPa; and flow rates of CO$_2$ of 5 and 20 g/min. The extraction process is cyclic. Each drying cycle lasts 40 min and the decompression time ranges from 5 to 60 min. The cyclic nature of the extraction process is determined by the need for the periodic evaluation of intermediate moisture values of wood samples. After each decompression step, the sample of wood is extracted from the drying chamber and weighed. The subsequent measurement of its mass is performed after a 30-min incubation of the sample at room temperature and atmospheric pressure. The amount of moisture that is removed from the sample is determined by weighing the water collected in the separator. The final moisture of the sample is determined for a given set of drying-process parameters after the kinetic curve reaches a time-independent value.

The experimental setup presented in Fig. 4 was developed to implement wood impregnation using a solvent in the supercritical fluid state.

After filling saturator *3* with the impregnating composition, heating is switched on, carbon dioxide is supplied, and the predetermined values of pressure and temperature are set. After passing through the saturator, CO$_2$ that contains a dissolved fungicide enters impregnation vessel *5*, where a sample of wood is placed. The impregnation vessel is equipped with electric heater *6* to maintain the required temperature. The pressure in the system is maintained by back pressure regulator *9*.

Samples are impregnated for 0.5, 1, or 3 h at a temperature of 338 K and pressures of 10, 20, and 30 MPa as CO$_2$ flows through the impregnation vessel at a con-stant flow rate (1 g/min). This makes it possible to carry out the impregnation process in the so-called "chromatographic" mode [16].

Wood samples for impregnation are cut from dried wood. Each sample has dimensions of 45 × 45 × 220 mm. If impregnation is carried out in the tangential direction from the beam end to the center (along the fibers), the side surfaces of the samples are insulated with epoxy resin so that only two beam ends remain uninsulated.

To determine the impregnation depth and the amount of substance deposited in the center of a sample, we used the method described in AWPA (American Wood Protection Association) Standard A23-94. Wood samples are sawed along the fibers (Fig. 5). After that, samples of 30 × 30 × 2 mm are cut from the cut-off region and the following five slices are taken: 0–22, 22–44, 44–66, and 66–88 mm. The selected samples are then ground to a state of wood powder after which 2.5 g of the wood powder from each slice is placed in 50 mL of methanol and incubated for six hours. The resulting extract is filtered and analyzed by chromatography according to the procedure described in AWPA A23-94. The separation is carried out on a Hypersil ODS (C 18) column of 10.0 × 4.6 mm with a 3-mm applied phase. Propiconazole is detected using a UV detector.

RESULTS AND DISCUSSION

A dynamic (flow) measurement method was used to determine the solubility of propiconazole in SC-CO$_2$. It is known [17] that the measurement results obtained by this method can be significantly affected by several factors, including the following:
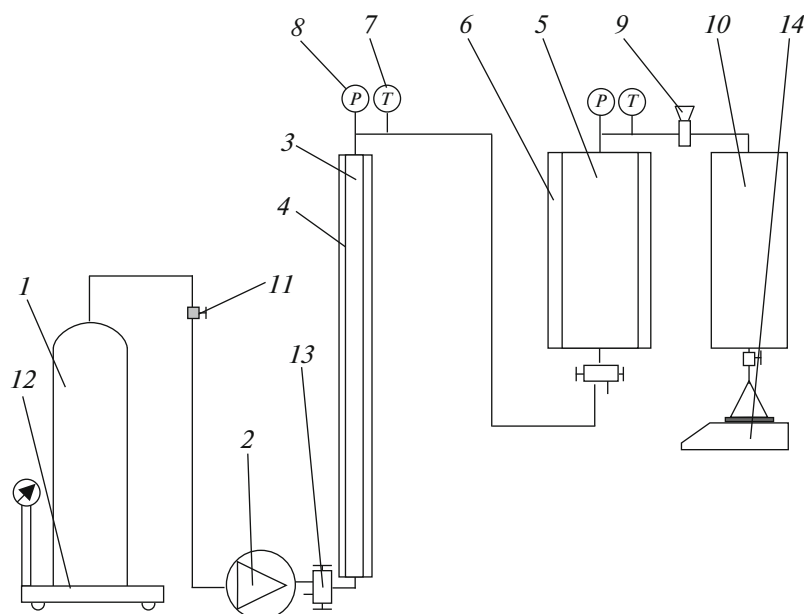
Fig. 4. Scheme of the experimental setup for the impregnation of wood using a solvent in the SCF state: *1*—CO_2 cylinder; *2*—pump; *3*—saturator; *4*—heater; *5*—impregnation vessel; *6*—heater; *7* and *8*—temperature and pressure sensors; *9*—back pressure regulator; *10*—separator; *11* and *13*—shut-off and regulating valves; and *12* and *14*—scales.
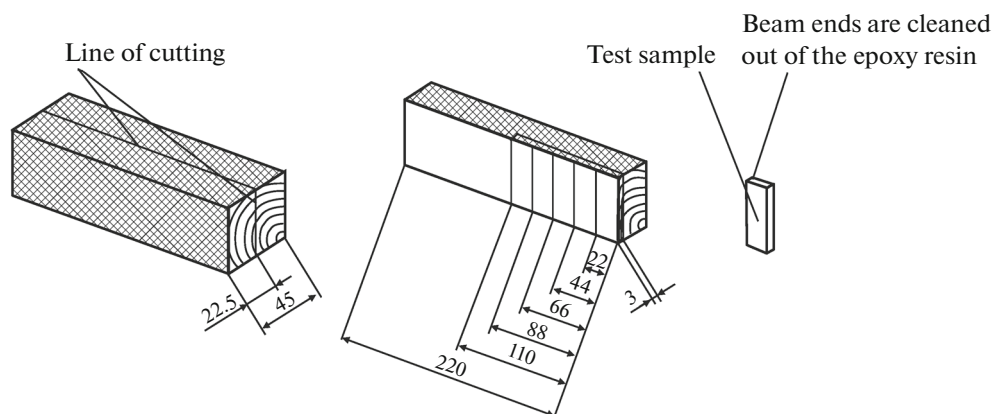

Fig. 5. Wood cutting scheme for the determination of the impregnation depth and the concentration of the impregnation composition in depth of the sample.

—taking a substantially nonequilibrium concentration of the solute in the flow of the SC fluid as the solubility;

—droplet entrainment with the stream of the solvent pumped through the extractor increases the value of the estimated solubility.

In the present work, we studied the effect of the SC-CO_2 flow on the concentration of propiconazole (Fig. 6) to reduce the significance of the above-mentioned factors. The solubility is taken to be the value that corresponds to a "plateau" of the propiconazole concentration dependence on the CO_2 consumption. Fig. 7 shows the results of measuring the propiconazole solubility in SC-CO_2 at 338, 358, and 378 K.

The solubility of propiconazole in CK-CO_2 at 358 K is generally consistent with the result obtained in [11] (353 K) within the total error of the measurement results, which is estimated to be 2.7—5.5% for the present study. At a lower temperature, however, the differences in the compared experimental data of the present study (338 K) and [11] (333 K) are 33%, which exceeds the assumed total error of the measurement results. This fact can be explained by the significant differences in the purity of the propiconazole used in this study (99%) and in [11] (88%). This conclusion was convincingly confirmed in [18] using the example of another fungicide (TCMTB).

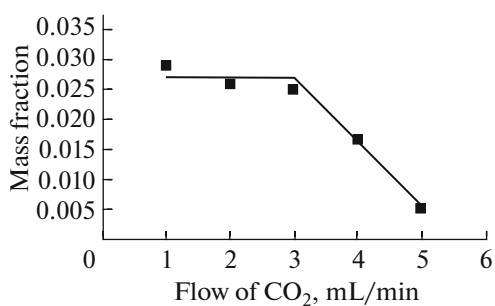Figures 8 and 9 show the results of the experimental study of the extraction drying of wood using SK-CO_2.

Fig. 6. Dependence of the concentration (mass fraction) of propiconazole in supercritical carbon dioxide on its consumption at 25 MPa and 338 K.
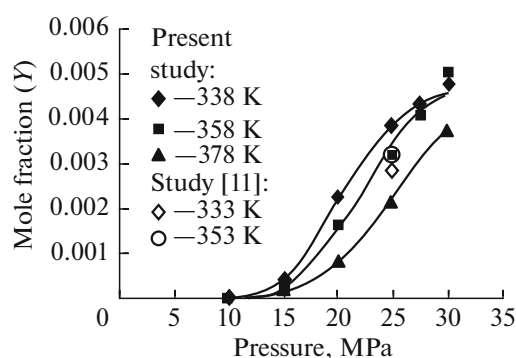

Fig. 7. Dependence of the mole fraction of propiconazole in its saturated solution in SC-CO$_2$ on the pressure. The flow rate of CO$_2$ is 2 mL/min.
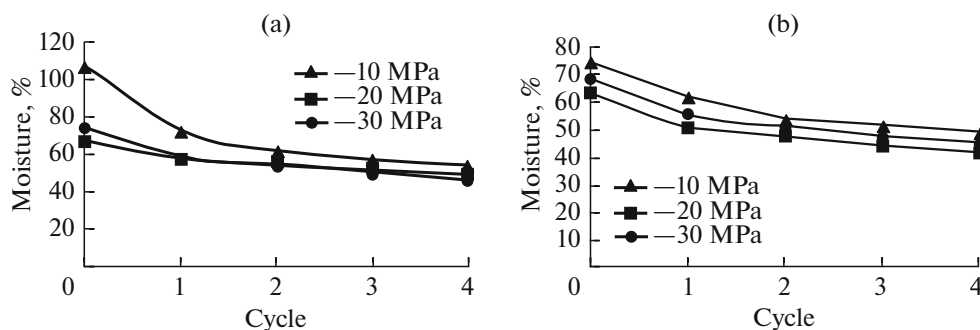

Fig. 8. Wood drying curves at a temperature of 323 K and pressures of 10, 20, and 30 MPa for different thicknesses of samples: a—50 mm; b—25 mm.

Figure 8 shows that the most intense removal of moisture from wood occurs in the first two cycles, after which the intensity decreases. 28−55% of moisture can be removed in the first cycle depending on the initial humidity.

The lower the initial wood moisture, the smaller the percentage of moisture that gets removed. For example, if the initial moisture content of the wood is 65−89%, the moisture of the sample can be decreased by 6−30% over the first cycle of drying. If the initial moisture content exceeds 90%, the moisture of the sample can be decreased by 40−55% over the first cycle of drying (Fig. 8a, 20 MPa). It should be noted that 40−87% of the moisture that can be removed from the wood is removed over the first cycle of drying.

Analysis of the results shows that after the wood moisture content decreases to 40−56%, the extension of the CS-CO$_2$ extraction drying becomes inadvisable because of the low moisture removal intensity.

Figure 9 shows the results of studying the effect of the drying-process parameters and the geometric dimensions of the samples on the efficiency of removing moisture from wood (based on the results of a single 60-min cycle). The following conclusions can be drawn from these data:

1. The effectiveness of the drying process (moisture removal) increases with increasing pressure, which is quite logical since this leads to an increase in the density of supercritical carbon dioxide and, consequently, in its extraction capacity. Minor deviations from this pattern (Fig. 9c; 343 K) fall within the limits of the total error of the measurement results for the compared experimental points and do not disprove the pattern. The nature of the anomalous change (minimum) of the moisture-removal efficiency at 30 MPa (Fig. 9c) and 343 K requires further investigation.

2. In the studied temperature range, the effectiveness of the drying process generally increases with increasing temperature. Moreover, this pattern holds even at a pressure of 10 MPa. A distinctive feature of this pressure is that its value lies between the pressure values at the first and second crossover points of an average substance dissolved in SC-CO$_2$ [19]. Thus, it would seem that this pressure should set the tendency of a decrease in the solubility with increasing temperature. However, the above-mentioned tendency does not hold for water dissolved in supercritical carbon dioxide [19], which determines the experimental pattern.

3. The drying process based on the use of SC-CO$_2$ modified with polar ethanol has its own peculiarities. In particular, in a moderate temperature range (up to
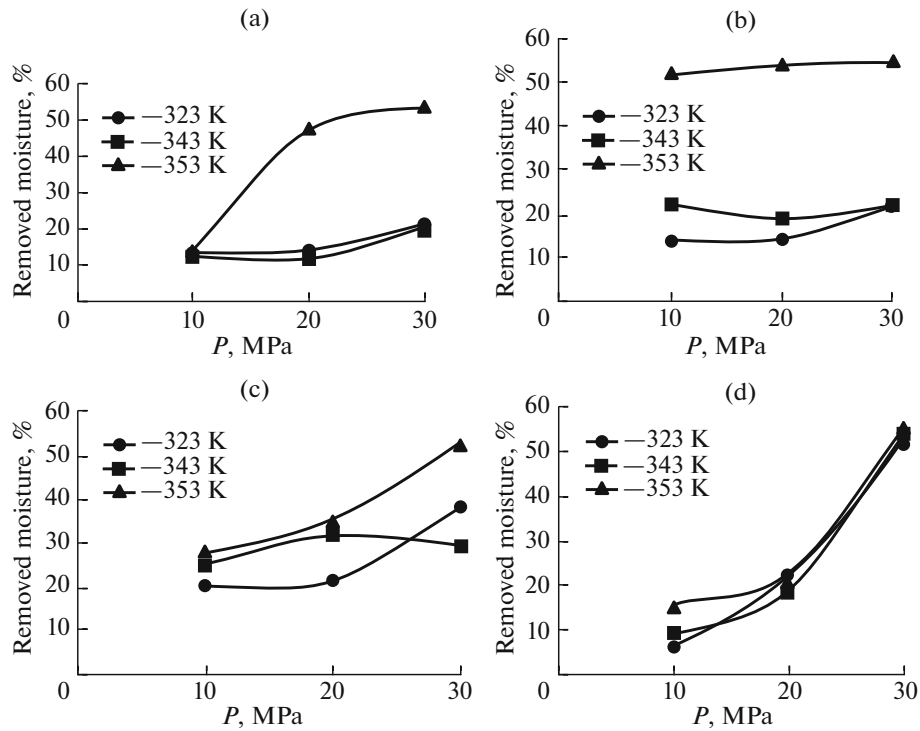
Fig. 9. Temperature dependence of the efficiency of moisture removal from wood samples of different thicknesses ((a and b) 50 mm; (c and d) 25 mm) by extraction with SC-CO_2 (a and c) and a CK-CO_2–ethanol mixture (b and d).
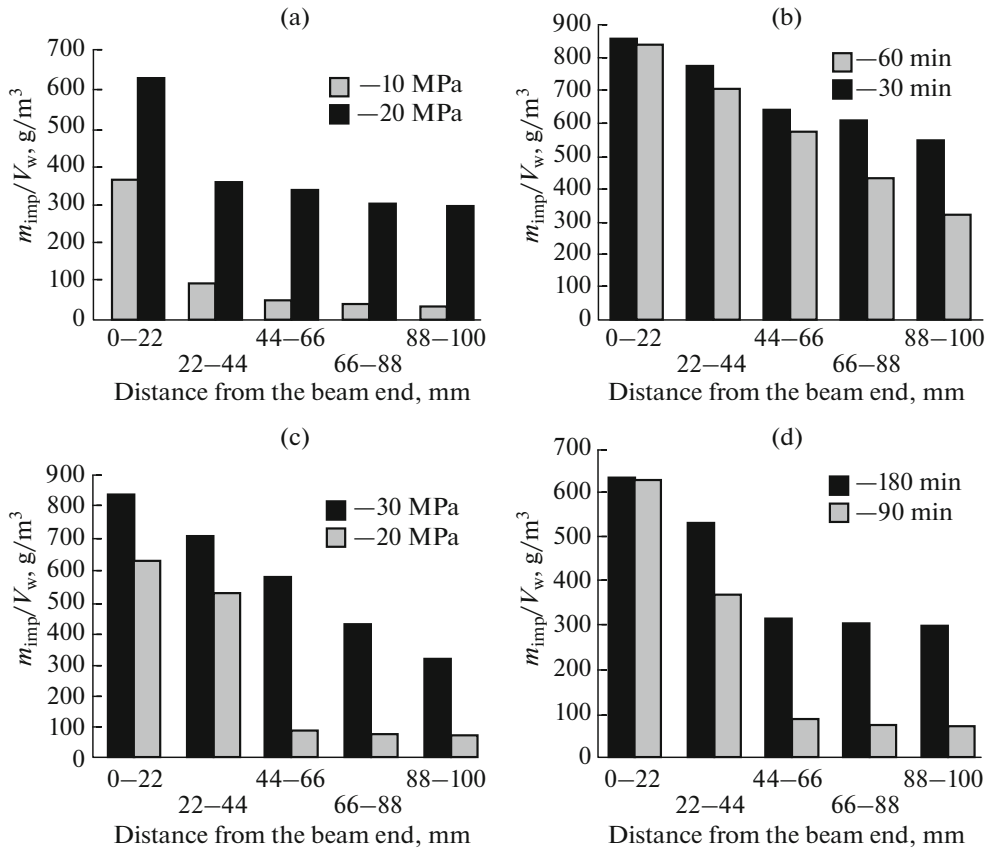

Fig. 10. Degree of wood impregnation with propiconazole at a temperature of 338 K: (a) pressures are 10 and 20 MPa and impregnation time is 180 min; (b) pressure is 30 MPa and impregnation times are 30 and 60 min; (c) pressures are 20 and 30 MPa and impregnation time is 30 min; and (d) pressure is 20 MPa and impregnation times are 30 and 180 min.

340 K), the efficiency of the modified extractant is expectedly enhanced for a 25-mm-thick sample at pressures of 20 and 30 MPa, whereas, for a 50-mm-thick sample, the expected efficiency can only be reached at 30 MPa. At elevated temperatures (above 350 K), the efficiency is expectedly enhanced for a 25-mm-thick sample at pressures of 20 and 30 MPa, whereas the expected elevated efficiency is virtually nonexistent in the case of a 50-mm-thick sample. The differences observed for samples of different thicknesses are caused by the fact that the duration of the drying process is the same in both cases. Thicker samples require longer drying. The lower efficiency of the modified extractant at relatively low pressures and temperatures is most likely due to the different phase states of the extractant components, which worsen the conditions of processing of the solid matrix.

Visual examination of the dried samples shows that cracks are formed on the samples of core wood even after the first drying cycle. The number and size of cracks on the core wood samples largely depend on the rate of the decompression process: the longer the decompression process, the fewer the cracks. No cracks were found in the sapwood samples.

Figure 10 shows the results of studying of the SC-CO_2-based process of wood impregnation.

CONCLUSIONS

The solubility of propiconazole in SC-CO_2 (mole fractions of 0.002–0.004 in the working pressure range of 20–25 MPa) is quite acceptable for the moderate energy consumption of the impregnation process. The value of approximately 10.0 MPa corresponds to the pressure at the first (lowest) crossover point of the propiconazole solubility, which stipulates a decrease in solubility with increasing temperature at high pressures up to the second (or highest) crossover point. In this study, we did not determine the pressure at the second crossover point.

The efficiency of the wood drying process implemented as a supercritical fluid extraction process with pure and modified CO_2 as an extractant generally increases with increasing pressure and temperature and in the presence of a polar solvent. The observed deviations from these regularities are due to the size factor of the wood samples, the peculiarities of the phase state of the modified extractant at relatively low pressures, etc.

The wood samples were thoroughly impregnated with propiconazole. The impregnation uniformity increases with increasing pressure and duration of the impregnation process.

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