Synthesis of Iso-amyl Ester Rosin and Its Evaluation as an Alternative to Paraffin in Medium Density Fiberboard Production

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Iso-amyl ester rosin was synthesized and investigated for its potential utilization in medium density fiberboard (MDF) production. The isoamyl alcohol, the main starting material for the synthesis of isoamyl ester rosin, was obtained through the fractional distillation of fusel oil, a byproduct of bioethanol production. The optimum condition for the iso-amyl ester rosin synthesis was determined as: rosin (165 mmol), isoamyl alcohol (413 mmol), P-TSA/rosin 1.5% (w/w), and commercial additive/rosin 0.15% (w/w). The esterification reaction was followed by FT-IR and mass analysis. For MDF production, a water-repellent material, commercial paraffin (1.5% w/w relative to the dry fiber weight), iso-amyl ester rosin (1.5% and 2.0%; w/w), and unmodified rosin (1.5% and 2.0% w/w) were separately used. In addition, fresh wood fibers, 10% w/w urea formaldehyde (UF) adhesive (relative to the total dry fiber weight), and a 25% aqueous solution of ammonium chloride (as the hardening agent for the UF adhesive, at 0.5% w/w based on the solid adhesive content) were used. MDFs underwent various physical and mechanical tests. Isoamyl ester rosin showed promising results based on the analysis. The results showed that the isoamyl ester rosin can be considered as an alternative to paraffin in sustainable and environmentally friendly MDF production.

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INTRODUCTION

Agro-industrial residues represent a valuable and sustainable asset for the material industry. Moreover, they have the potential to serve as a basis for the production of various chemicals. These products can be converted into high-value chemical compounds, offering the potential to substitute for petroleum-derived compounds. An illustrative case involves the production of alcohols through fermentation (de Jesús Mendoza-Pedroza *et al*. 2021).

Over time, the industrial production of ethanol through fermentation has seen significant growth, driven by the increasing global need for biobased chemicals. The current market valuation stands at around 33.7 billion USD, and it is projected to reach USD 64.8 billion by 2025. This process has emerged as a significant focal point in enhancing sustainability within the production cycle. The potential for employing by-

products from agro-industrial waste treatment has opened up substantial opportunities for reducing waste and generating direct revenue (Pimentel-Moral *et al*. 2020).

Among the various by-products of ethanol production, fusel oil (FO), also known as fusel alcohol or simply fusel, has emerged as a compelling source of higher-value chemicals. FO is a blend of alcohols, including iso-amyl alcohol, ethanol, iso-butanol, and propanol, along with water. The chemical composition of FO varies depending on the raw material used for alcohol production in fermentation, such as sugarcane, barley, corn, rice, and sugar beet, as well as the effectiveness of its separation from the fermented mixture (Massa *et al*. 2023).

FO boasts a significant isoamyl alcohol content, ranging from 57.65% to 74%, making it a suitable acyl acceptor for trans-esterification reactions (Dias *et al*. 2018; Simsek and Ozdalyan 2018; Dias *et al*. 2020). This property allows it to be utilized in the production of esters with flavor-enhancing characteristics (Dias *et al*. 2018; Tran *et al*. 2020), biolubricants (Cerón *et al*. 2018), and fuel applications (Tebas *et al*. 2021). In particular, isoamyl acetate finds wide application as a "green solvent," serving as a substitute for methyl ethyl ketone. It is also utilized as an additive in nitrocellulose lacquers and as a flavoring agent, imparting banana flavors (Welsh *et al*. 1989; de Jesús Mendoza-Pedroza *et al*. 2021).

In recent years, alongside the utilization of biobased waste materials, the production of biobased products through sustainable practices has gained significance. The use of these products is increasingly driven not only by their sustainability and biobased nature but also environmental and health concerns. These circumstances are increasing the demand for the usage of biobased sustainable products. One of the best examples of biodegradable and sustainable materials is rosin.

Rosin has found applications in various fields from the past to the present. Rosin is a complex substance derived from different types of natural resins (Hawley and Palmer 1912). Rosin has a vast of applications in various fields, including paints, varnishes, and coatings (Scalarone *et al*. 2002; Echard *et al*. 2010; Tirat *et al*. 2016). Today, there is a growing exploration of new application areas such as composite technology (Gennusa *et al*. 2017). This interest is driven by the biobased and biocompatible nature of rosin (Barabde *et al*. 2005).

The chemical nature of natural rosin consists of diterpenic acids, making up 90% of its composition, while the remaining 10% is a combination of esters, alcohols, aldehydes, and hydrocarbons. Resin acids can be categorized into two main types: abietic and pimaric acids, and within each of these acid groups, there are various isomeric compounds (Cabaret *et al*. 2019). The structure of resin acids includes a tricyclic framework with two double bonds and a carboxylic functional group. This particular structural feature makes rosin amenable to chemical modifications, allowing for the creation of a wide array of derivatives, including polymerizable structures suitable for different types of materials (Liu *et al*. 2011). Rosin is rigid and prone to be brittle. It does not dissolve in water but readily dissolves in acids and a wide range of organic solvents (Yadav *et al*. 2016). It offers numerous benefits to the materials industry due to its abundant natural availability, cost-effectiveness, and its ease of conversion into high-performance macromolecular materials. The hydrophobic nature of rosin allows for its use as a substitute of water-repellent petrochemical-derived chemicals. Derivatives of rosin can be employed to create polymers by blending them with conventional monomers, allowing for the adjustment of the characteristics of the final material (Gandini and Lacerda 2015).

Medium density fiberboard (MDF), a wood-based panel comprising of lignocellulosic fibers, is manufactured using synthetic resins or alternative bonding systems, subject to varying temperature and pressure conditions. MDF is widely employed in construction, it serves as panels, insulating materials, and coverings. It is preferred more than particleboard, plywood, and solid wood in numerous furniture applications (Ye *et al*. 2007; Gürgen *et al*. 2019). The preference for MDF production over other wood-based materials is primarily attributed to the utilization of forest residues and other industries by-products as a raw material. This stands in contrast to solid wood, making MDFs an environmentally friendly choice by repurposing waste materials in its production (Akgül and Çamlibel 2008; Moreno-Anguiano *et al*. 2022).

The aim of this study is to investigate the use of iso-amyl ester rosin, as a water-repellent chemical in the medium density fiberboard (MDF) industry, instead of paraffin. In this work, the synthesis of iso-amyl ester rosin, and its application as a hydrophobic material in MDF production are reported for the first time. Iso-amyl ester rosin serves as an eco-friendly multifunctional additive.

EXPERIMENTAL

Materials

Resin from *Pinus pinaster* was used in this study. For the esterification reactions, P-TSA purity, ≥ 98.5% (Sigma-Aldrich, St. Louis, MO, USA), commercial additive Irganox 1010, Pentaerythritol tetrakis[3-[3,5-di-*tert*-butyl-4-hydroxyphenyl]propionate (CAS Number: 6683-19-8; free of charge from BASF, Türkiye) was obtained. Fusel oil was procured from Amasya Sugar Factory Inc. (Türkiye). Na_2SO_4 (purity ≥ 99.0 %). Na_2SO_4 was obtained from Akkim Chemistry Industry and Trade Inc. (Türkiye). Medium Density Fiberboard (MDF) production was carried out at the Kastamonu Integrated Wood Industry R&D Laboratories (Türkiye). Therefore, the necessary chemicals for panel production (paraffin, UF adhesive, wood fibers (beech and pine), ammonium sulfate) were provided by the company. Due to confidentiality requirements, the brand names and types of the inputs included in the formulation content of MDFs were not revealed.

Distillation of Pine Resin

The resin distillation study was conducted with temperature control. The production of rosin from natural pine resin was obtained using the simple distillation method. A total of 500 g pine resin was taken in a three-necked 1.0-L reaction flask and a simple distillation method was started by adding 50 mL distilled water. Temperature was increased in a controlled manner during the distillation. When the temperature reached 80 °C, turpentine flow started and lasted for about 3 h. At the end of the distillation, the rosin was poured into aluminum containers and stored in a dark place (Yılmaz 2023).

Extraction of Fusel Oil

This work was started with filtration studies to remove impurities of FO before fractionation. The FO was passed through ordinary filter paper, such that impurities were removed. Then, some amount of Na_2SO_4 was added to eliminate the moisture and it was mixed homogeneously overnight using magnetic stirring without heating. Then, FO was filtered and passed through molecular sieve to remove water. Following the impurity and water removal processes, fractionation studies were started. Fractions were obtained at 4

different temperature ranges (78 to 80, 80 to 97, 97 to 100, and 100 to 105 °C) (Güvenç *et al*. 2007).

Gas Chromatography-Flame Ionization Detection (GC-FID) of Fusel Oil and Its Fractions

Analysis using GC-FID was conducted at Recep Tayyip Erdoğan University Central Laboratory. The GC-FID studies were performed using SPME (solid phase micro-extraction) method on a Shimadzu GC-MS-QP2010 using Rxi-5MS column. Column temperature was kept at 40 °C, and the injection temperature used was 250 °C. Analysis conditions were 2 min at 40 °C, followed by ramping from 40 to 240 °C at a rate of 4 °C/min. Total analysis time was 52 min.

Synthesis of Isoamyl Ester Rosin

About 50 g (165 mmol) pine rosin was placed in a 250-mL three-necked reaction flask, and 13.36 mL isoamyl alcohol (413 mmol), 1.5% (w/w) P-TSA/rosin and 0.15% (w/w) commercial additive (Irganox 1010)/rosin were added. Irganox 1010 was used to accelerate the esterification reaction between isoamyl alcohol and rosin and to ensure the stability of the product by protecting the material against high temperatures. While the esterification reaction was in progress, the acid number standard test using ASTM D465-05 (2010) was applied by taking samples from the reaction media. In addition, FT-IR analysis was also performed to detect chemical transformations during the reaction time. Additionally, mass analysis of the synthesized product has been conducted to determine its mass, thus confirming the formation of the iso-amyl ester rosin. The reaction scheme related to the synthesis of isoamyl ester from rosin is depicted in Fig. 1.

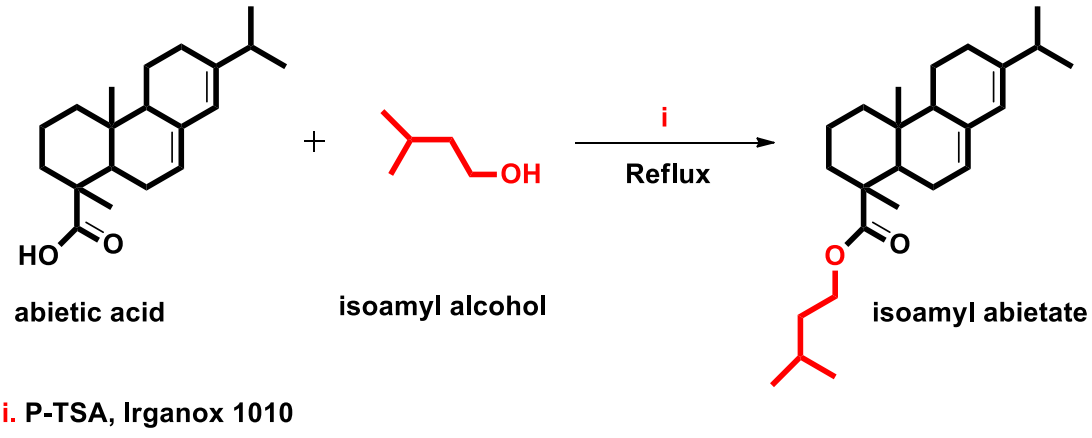


Fig. 1. Synthesis of iso-amyl ester rosin

Fourier-Transform Infrared (FT-IR) and Liquid Chromatography-Mass Spectrometry (LC-MS/MS) Analysis

The FT-IR analyses were carried out using a Perkin Elmer Frontier Model instrument (Waltham, MA, USA). Spectra were recorded at a resolution of 4 cm^{-1}, spanning the range from 4000 to 500 cm^{-1}.

Mass spectroscopical analyses were conducted using a Thermo (Model TSQ Quantum Access) LC-MS/MS instrument.

Medium Density Fiberboard Production

Medium Density Fiberboard production was carried out at the Kastamonu Integrated Wood Industry R&D Laboratories. In this study, commercial beech-pine fibers were utilized as a raw material for MDF production. The fiber mixture ratio was determined as 60% beech and 40% pine. Fibers were dried in a laboratory oven until they reached a moisture content of 8%. The inputs used in the developed MDF within the scope of the study have remained unchanged, except for the material used for imparting water repellent properties. The ratios of paraffin and substitute materials are provided in Table 1. In the study, five different fiberboards were produced. Three fiberboards were produced from each MDF, and a total of 15 MDFs were produced."

Table 1. Medium Density Fiberboards and their Contents

MDF	Content
MDF 1	Paraffin, 1.5%
MDF 2	Rosin, 1.5%
MDF 3	Rosin 2.0%
MDF 4	Iso-amyl ester rosin, 1.5%
MDF 5	Iso-amyl ester rosin, 2.0%

Urea-formaldehyde (UF) was taken as adhesive at 10% ratio. Paraffin emulsion (with a solid content 37%) was added as a control to UF adhesive at weight ratio of 1.5% (MDF1). Iso-amyl ester rosin was added with UF adhesive at ratio of 1.5% (MDF2) and 2.0% (MDF3) and also unmodified rosin 1.5% (MDF4) and 2.0% (MDF5), and ammonium chloride aqueous solution (25%) was used in an amount equivalent to 0.5% of solid adhesive as a hardener.

The fibers were placed in thickness boards around their edges before pressing. The preform was prepared within a 500 × 500 mm^2 frame, and cold pressing was applied to the laid fibers to create the preform before pressing. Optimization studies were conducted to determine the pressing conditions to produce ideal MDFs. The most optimal conditions were achieved for an 8 mm board with a maximum pressing pressure of 3.5 N/mm^2, a press plate temperature of 210 °C, and a pressing time in the range of 200 to 210 s. The board thicknesses, including the allowance for sanding, were adjusted to achieve a gross board thickness of 8.5 to 9 mm after pressing. The moisture content of the boards upon exiting the press was determined to be 6% to 7%. Thickness measurements were conducted using an electronic caliper after the pressing process. The moisture content of the MDF panels was calculated according to the EN 323 standard.

Moisture Content

TS-EN 322 (1999) was taken as a basis when determining the amount of moisture. The samples were weighed on a precision balance with a sensitivity of 0.01 g. The prepared samples were placed in a drying cabinet and dried at 103 ± 2 ºC until a constant weight was reached. After reaching the constant mass, the samples were weighed again on a precision balance with a sensitivity of 0.01 g and calculated using Eq. 1,

$$M = \frac{mr - m0}{m0} x100 \quad (1)$$

where m_r is sample initial weight (g) and m_0 is dry sample weight (g).

Water Absorption and Thickness Swelling

The water absorption (WA) and thickness swelling (TS) of the MDF samples after 24 h of immersion in water were determined in accordance with EN 317 (1993). Samples each measuring 50 mm × 50 mm, were cut from the boards and used for the WA and TS measurements. Initially, the weight and thickness of all samples were measured. Subsequently, these samples were immersed in water at a temperature of 20 ±2 °C. At the conclusion of each immersion period, the final thickness and weight of the samples were recorded. The WA and TS of the MDF samples were calculated using Eqs. 2 and 3,

$$WA\ (\%) = \frac{W2-W1}{W1} x100 \quad (2)$$

$$TS\ (\%) = (T2-\ T1)\ /\ T1\ x\ 100 \quad (3)$$

where W_2 is the MDF weight after immersion (g), and W_1 is the MDF weight before immersion and T_2 and T_1 are the thickness after and before immersion (mm), respectively.

Mechanical Tests

Modulus of rupture (MOR) and modulus of elasticity (MOE)

The MOR test was conducted in accordance with the TS EN 310 (1999) standard. For the determination of MOR, four samples were taken from each board. The samples were prepared with dimensions of 41 × 5 cm^2. Thicknesses were measured at two points along the loading line with a caliper sensitive to 0.01 mm, and the average was calculated. The bending resistance test was conducted on the IMAL Universal testing machine. The measurements were calculated using Eq. 4,

$$MOR = (3\ x\ F\ x\ L)\ /\ (2\ x\ b\ x\ d^2) \quad (4)$$

where F is the peak load (N), L is the distance (mm), b is the sample width (mm), and d is the sample thickness (mm).

The MOE test was conducted according to the TS EN 310 (1993) standard. For the experiment, samples measuring 250 × 50 × 20 mm^3 were prepared and kept in a climate-controlled environment until they reached a constant weight. The amount of bending in the elastic deformation region was determined. For this purpose, the displacement gauge of the Universal Testing Machine was used. Elastic deformation was measured with a sensitivity of 0.01 mm, and the force at the point of fracture was determined with a sensitivity of 1 kgf. After the experiment, the elastic modulus (EM) of each sample was calculated using Eq. 5,

$$MOE = (F\ x\ L^3)\ /\ (4\ x\ \Delta e\ x\ b\ x\ d^3) \quad (5)$$

where F is the applied force causing deformation (kgf), L is the span between support points (cm), b is the width of the sample (cm), d is the thickness of the sample (cm), and Δe is the amount of bending (cm).

Internal Bonding

The tensile strength perpendicular to the surface of the plate were conducted in accordance with the standard provided in TS EN 319 (1999). For each group, 12 samples with dimensions of 50 × 50 mm^2 were prepared. An IMAL testing machine was used to perform tensile strength tests perpendicular to the surface of the plate. The samples were placed between the gripping points of the testing machine, and a tensile force was applied to fracture them. The rate of movement of the force applicator was adjusted to remain

constant throughout the test, and it was set to reach the maximum force that would fracture the test specimen in 60 ± 30 s. The maximum force that caused the specimen to fracture was measured with 1.0% accuracy. The internal bonding was calculated according to Eq. 6,

$$F_t = F_{max}/a * b \quad (6)$$

where F_{max} is the maximum tensile load (N) and *a, b* are the length and width of the test specimen (mm), respectively.

RESULTS AND DISCUSSION

Rosin Yield and Its Properties

The production of rosin was completed with a yield of 75% according to the ASTM D465-05 (2010) standard. The acid number of rosin was determined as 160 mg KOH/g. The yield of rosin is influenced not only by the distillation method but also by production time (year and month), resin production method, location of resin production, and tree species used in resin production. Deniz and Hafızoğlu (1989) determined the quantity of rosin obtained from red pine resin as 68.4% to 78.8%. Yılmaz (2023) reported maritime pine rosin average yield as 75.0%. As known, rosin contains a high amount of resin acids in its composition, which is why its acid number value is typically high (Yılmaz 2023). Natsir *et al*. (2021) reported the acid value of *Pinus merkusii* rosin as 175 mg KOH/g.

GC Analysis of Fusel Oil and Its Fractions

The chemical characterization of FO before the separation is presented in Table 2. Iso-amyl alcohol was determined as 26.2% by area percentage. Güvenç *et al*. (2007) determined iso-amyl alcohol at 54.1% level before the separation of fusel oil *via* GC analysis. The raw material used in bioethanol production and the bioethanol production process are crucial in determining the chemical content of fusel oil.

Table 2. GC-MS Analysis of Fusel Oil

No	Retention Time (min)	Area (%)	Component
1	1.4201	15.6409	Methane
2	1.4746	33.0679	Ethanol
3	1.5537	12.4704	1-Propanol
4	1.6457	11.9863	2-Methyl-1-propanol
5	1.7137	0.6848	1-Butanol
6	1.9203	26.1497	Iso-amyl alcohol

The results of the GC analysis of fractions obtained at four different temperature stages (78 to 80 ℃, 80 to 97 ℃, 97 to 100 ℃, and 100 to 105 ℃) through fractional distillation of fusel oil are presented in Tables 3 and 4. After the fractionation studies, iso-amyl alcohol content was enriched.

In Table 3, it was determined that in the 78 to 80 °C fraction, 2-methyl butyraldehyde is a degradation product of iso-amyl alcohol. The quantity percentage of iso-amyl alcohol was determined as 42.0% by area percentage. For the 80 to 97 °C fraction, 2-methyl butyraldehyde and 3-methyl butanol were identified as decomposition products

of iso- amyl alcohol, and the total area of iso amyl alcohol was 92.4%. This fraction was utilized in the esterification studies of rosin. Güvenç *et al*. (2007) detected 54.1% iso-amyl alcohol in the initial stage of fusel oil analysis. As a result of the fractional distillation of fusel oil, they determined the yield of iso amyl alcohol-enriched fraction (at 128 °C) as 99.7%.

Table 3. The GC-MS Analysis Results for the 78 to 80 °C and 80 to 97 °C Fractions

	78 to 80 °C			80 to 97 °C		
No	RT (min)	% Area	Component	RT (min)	% Area	Component
1	3.151	22.47	Iso-amyl alcohol	2.935	57.49	2-Methyl butyraldehyde
2	3.214	19.58	2-Methyl butyraldehyde	3.180	3.37	3-Methyl butanol
3	6.805	57.95	2,4-Dimethyl benzaldehyde	3.236	31.53	İso-amyl alcohol
4	-	-	--	4.781	1.77	2-Methyl-3H-pyran-4-one
5	-	-	--	8.023	5.84	Piperazine derivatives
Total		100			100	

Table 4. The GC-MS Analysis Results for the 97 to 100 °C and 100 to 105 °C Fractions

	97 to 100 °C			100 to 105 °C		
NO	RT (min)	% Area	Component	RT (min)	% Area	Component
1	3.243	68.45	Isoamyl alcohol	8.101	88.94	2,4-Dimethyl benzaldehyde
2	4.749	3.53	2-Methyl-3H-furan-3-one	14.740	11.06	Valeraldehyde
3	7.940	26.27	Piperazine derivatives	-	-	-
4	21.06	1.75	2-Phenethyl acetate	-	-	-
Total		100			100	

FT-IR and LC MS-MS Analysis Results

The FTIR spectra of gum rosin (GR) and iso-amyl ester rosin are shown in (IAER) Fig. 2.

According to FT-IR spectra, the peaks at 2872, 2881, 2927, and 2956 cm^{-1} are characteristic of aliphatic C-H bond stretching within the structure. The peaks at 1245 and 1252 cm^{-1} were attributed to C-O-C stretching vibrations within the -COOH group (Wang *et al*. 2016). After the esterification, it was observed that the characteristic bond for the carbonyl compound of carboxylic acid (C=O, 1688 cm^{-1}) was shifted to ester carbonyl peak (C=O, 1720 cm^{-1}). It has been determined that the carbonyl peak of carboxylic acid transformed into an ester carbonyl peak. The presence of the ester carbonyl peak in the FT-IR spectrum indicated that the esterification reaction was successfully carried out.

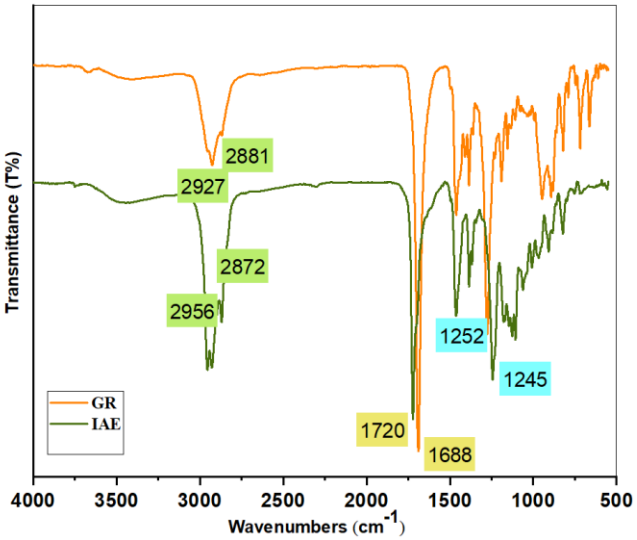
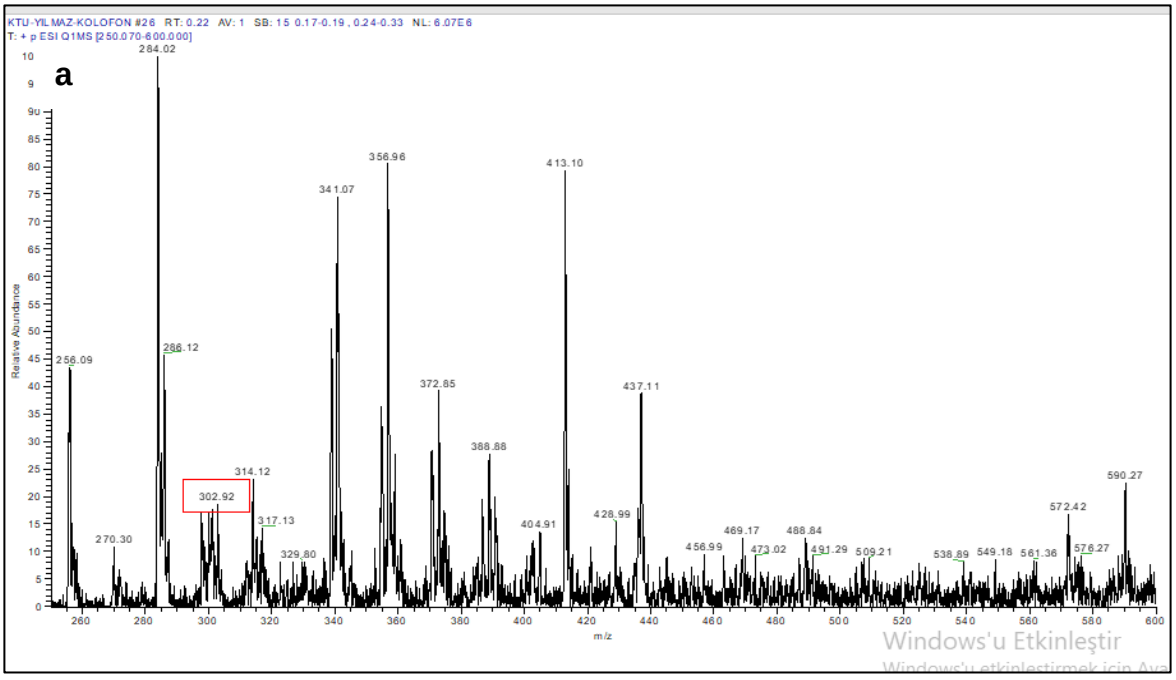


Fig. 2. FT-IR spectra of the gum rosin and isoamyl ester rosin

The mass analysis results for gum rosin and iso-amyl ester rosin are presented in Fig. 3. In the analysis, abietic acid was identified with a mass-to-charge ratio (*m*/*z*) of 302.92 in pine rosin. Rosin is composed of approximately 90% to 95% resin acids and around 5% to 10% alcohols, aldehydes, and hydrocarbons (Karlberg 2000; Wiyono *et al*. 2006). The most commonly found resin acids in pine rosin are abietadienes (abietic, levopimaric, palustric, and neoabietic) and pimaradienes (pimaric, isopimaric, and sandaracopimaric acid) (Valto *et al*. 2012; Cabaret *et al*. 2018). The mass of isoamyl ester of rosin, resulting from the reaction of abietic acid with isoamyl alcohol, was determined as 373. After the esterification reaction, a noticeable increase in molecular mass was observed.



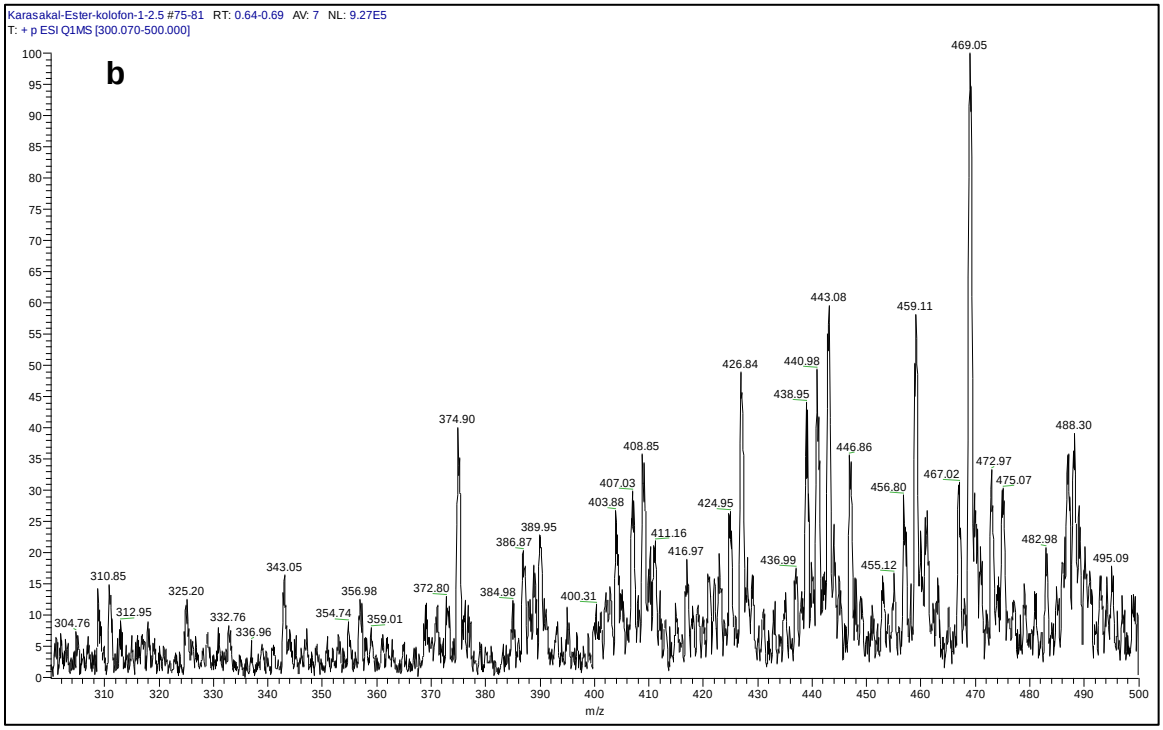


Fig. 3. LC-MS/MS analysis of a: Gum rosin, b: Iso amyl ester rosin

Physical and Mechanical Properties of MDFs

The results from TS and WA analyses are presented in Table 5. The TS (24 h) and TS (2 h) averages of the data were determined, which ranged between 24.0% and 34.4%. The best results in terms of TS (24 h) were achieved by MDFs that used iso-amyl alcohol (2.0% w/w, MDF5) and also paraffin (1.5% w/w, MDF1) as a water repellent product. The highest TS was observed in MDF2. Based on the WA (24h) results, MDFs produced with 2.0% iso-amyl ester rosin were much better than paraffin (50% to 53%). The TS and WA results indicated that the addition of isoamyl ester rosin (2.0%) into the UF resin, enhanced the hydrophobic properties of the structure. This is an expected result due to the chemical structure of rosin compound. In addition to this, it was observed that the hydrophobic property of rosin increased after modification with iso-amyl alcohol.

Boards produced with unmodified rosin demonstrated higher levels of TS and WA compared to the other boards. However, when examined within itself, it was found that as the amount of unmodified rosin was increased, the TS value decreased. It was concluded that the increasing the amount of rosin and modified rosin within the MDFs statistically significantly enhanced the hydrophobic properties of MDFs.

Table 5. Physical Properties (swelling and water uptake) of the MDFs

MDFs		WA-24h (%)	TS-24h (%)	TS-2h (%)
MDF1	Ave. St.D	53.00 (2.73)^{b}	24.00 (2.29)^{a}	12.24 (0.89)^{a}
MDF2	Ave. St.D	63.52 (2.17)^{d}	34.44 (2.12)^{b}	18.33 (0.92)^{c}
MDF3	Ave. St.D	66.23 (1.69)^{e}	33.00 (2.17)^{b}	17.95 (0.57)^{c}
MDF4	Ave. St.D	61.00 (2.34)^{c}	25.00 (3.00)^{a}	13.52 (0.65)^{b}
MDF5	Ave. St.D	50.00 (0.50)^{a}	24.00 (1.58)^{a}	12.80 (0.62)^{a}

Some physical and mechanical properties of MDFs are presented in Table 6 According to the results, with the addition of iso-amyl ester rosin in the production of MDFs, the density of MDF decreased. It can be seen from Table 6 that the average density of the MDFs ranged from 799 to 933 kg/m^3. Because of the iso amyl ester rosin having a chemical structure different from the paraffin, it can be stated to influence the final product density.

Table 6. Some Physical and Mechanical Properties of MDFs

MDFs		Density (kg/m^3)	Moisture (%)	IB (MPa)	MOE (MPa)	MOR (MPa)
MDF1	Ave. St.D	906.00 (15.87)^{d}	5.10 (0.36)^{d}	1.66 (0.07)^{d}	2860.00 (63.04)^{d}	35.00 (2.59)^{b}
MDF2	Ave. St.D	799.45 (12.58)^{a}	4.35 (0.26)^{c}	0.60 (0.04)^{a}	2546.66 (97.45)^{b}	36.00 (2.12)^{b}
MDF3	Ave. St.D	934.50 (14.95)^{e}	4.50 (0.30)^{c}	0.63 (0.03)^{a}	2305.33 (66.20)^{a}	32.66 (2.50)^{a}
MDF4	Ave. St.D	878.00 (11.74)^{c}	4.00 (0.27)^{b}	1.01 (0.11)^{c}	2623.00 (56.46)^{c}	34.00 (2.06)^{ab}
MDF5	Ave. St.D	813.00 (10.90)^{b}	3.50 (0.22)^{a}	0.70 (0.41)^{b}	2903.00 (61.76)^{d}	39.00 (2.17)^{c}

The average MOE of MDFs ranged from 2300 to 2900 N/mm^2. The MOE was highest in MDF5 (2.0% iso-amyl ester rosin) among the MDFs. This result revealed that isoamyl ester rosin did not only impart water repellent properties of MDFs but also improved their mechanical characteristics.

The average IB of MDFs ranged from 0.60 to 1.66 N/mm^2. The increase in the amount of iso amyl ester rosin led to a decrease in IB values. The IB was determined as 1.01 N/mm^2 in MDF4 board, while in MDF1, it was 1.66 N/mm^2. This implies that the excessive presence of iso-amyl ester rosin within the structure can reduce the internal bonding. However, the IB of the panels align with the literature.

The average MOR of MDFs ranged from 32.7 to 39.0 N/mm^2. An improvement in MOR was reported in MDFs produced with modified rosin (2.0%). Moreover, MOR results were detected statistically similar in MDFs produced with unmodified rosins and paraffin.

The TS 64-5 EN 622 (1999) standard suggests that MDFs intended for general-purpose use should have a minimum MOE value of 2200 N/mm^2 and a minimum IB

strength value of 0.55 N/mm^2. The current results indicate that all the manufactured MDFs met the specified minimum criteria.

CONCLUSIONS

In this study, the use of isoamyl ester rosin was investigated as an alternative to paraffin as a hydrophobic material in the production of medium density fiberboard. The iso-amyl alcohol was obtained through the fractional distillation of waste FO generated during bioethanol production. In addition to the valorization of waste materials, the main synthesis product bio-based rosin aligns with sustainability goals. The results of the study support the use of iso-amyl ester rosin as a hydrophobic material in MDF production. The results obtained in the study are summarized as follows:

1. The esterification reaction between isoamyl alcohol and rosin was confirmed by FT-IR spectra. The carbonyl peak in carboxylic acid was observed at 1688 cm^{-1} that was shifted to 1720 cm^{-1} after the esterification reaction.
2. The esterification reaction was also supported by LC-MS/MS analysis. The molecular mass of unmodified rosin was determined as 302.42 g/mol, whereas molecular weight of the isoamyl ester rosin was 430.54 g/mol. The increase in mass is directly proportional to the molecular growth.
3. The iso amyl ester rosin (2.0%) noticeably reduced water absorption and improved the dimensional stability of the MDFs.
4. The MDFs produced with the addition of iso-amyl ester rosin at a level of 1.5% exhibited the best performance compared to the control board in terms of internal bonding value. It was observed that the additional inclusion of iso-amyl ester rosin did not have a significant impact on inter-fiber bonding.

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