Partial and Total Solvent-Free Limonene’s Hydrogenation: Metals, Supports, Pressure, and Water Effects

Fanta J. Ndongou Moutombi,1 Anne-Sylvie Fabiano-Tixier,2 Olivier Clarisse,1 Farid Chemat,2 and Mohamed Touaibia1

1Department of Chemistry and Biochemistry, Université de Moncton, Moncton, NB, Canada
2Université d’Avignon, INRA, UMR408, GREEN Extraction Team, F-84000 Avignon, France

Correspondence should be addressed to Mohamed Touaibia; mohamed.touaibia@umoncton.ca

Received 1 November 2019; Revised 4 February 2020; Accepted 10 March 2020; Published 1 April 2020

Academic Editor: Ioannis D. Kostas

Copyright © 2020 Fanta J. Ndongou Moutombi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Bio-based solvents menthene and menthane were obtained through limonene’s partial and total hydrogenation under various catalytic conditions. Heterogeneous catalysts based on different active metals and supports (carbon, alumina, and silica) were systematically tested for solvent-free total and partial hydrogenation of limonene under high and low hydrogen pressure. Influences of these catalysts on the formation of menthene, menthane, and cymene, a dehydrogenated product, were determined. The impact of water addition on the conversion and selectivity of the catalysts was also investigated. Amongst all tested catalysts, Rh/Alumina which was never tested for total and partial hydrogenation of limonene was the most effective as 1-menthene was quantitatively produced at low pressure (0.275 MPa) while menthane was mostly obtained at a higher pressure (2.75 MPa). Water addition on Rh/Alumina favoured menthene production even at high pressure. To propose menthene, menthane, and menthene/menthane mixture as an alternative to fossil-based solvents such as n-hexane for the extraction of natural products, β-carotene, vanillin, and rosmarinic acid solubilizations have been investigated. If a modeling approach using COSMO-RS software predicted a comparable solubilization of these 3 compounds for the 3 solvents, experimental assays revealed that menthene solubilizes β-carotene, vanillin, and rosmarinic acid three to five times better than n-hexane.

1. Introduction

Nature wastes that were previously neglected are now recognized as precious materials. Plants, essential oils, and citrus peel constitute abundant and renewable biomasses with added value; they are inexpensive precursors that bring interesting properties to various industrial applications [1]. Limonene, a monocyclic terpene, and its hydrogenation products are part of this category of natural organic compounds. Nowadays, the literature reports several examples of the use of these products in pharmaceutical, cosmetics, food, and agrochemical processes [2, 3]. Thus, research on the valorization of the limonene molecule, in particular by hydrogenation reactions, is of particular interest [4]. Indeed, the high reactivity of this molecule which can itself be a source of hydrogen makes its selective transformation difficult [5]. According to Augustine, the hydrogenation of limonene carbons corresponds to a type II selectivity, since it is possible to obtain two distinct products by two parallel reactions: p-menthene (product of the partial hydrogenation) and p-menthane (product of the total hydrogenation) starting from the same starting material [6, 7] (Scheme1).

p-Menthene, also known as carvomenthene, has been identified as an attractive building block for many chemicals such as pharmaceuticals, agrochemicals, perfumes, and bioplastic monomers [8, 9]. The p-menthene’s potential is due to the retention of the chiral centre and the intracyclic double bond that can be functionalized. p-Menthene has been used as a starting material for the synthesis of many practical products, such as endoperoxides and (−) menthol, widely used in pharmacy and in the development of pesticides [10–12]. p-Menthene is also used as a food scent in...
fruit juices and other food products and since a long time in
glues, adhesives, and resin synthesis process [13, 14].

\( p \)-Menthan, which is a flavouring compound, is present
for instance in peppermint [15]. This fully hydrogenated
product has been shown to be a promising aviation biofuel
and diesel fuel additive [16–19].

Starting from pure limonene without organic solvent or
water, heterogeneous catalytic for total or partial hydrogena-
tions has been previously reported: over Pd on porous glass
catalyst system at room temperature and atmospheric pres-
sure, menthane was obtained by Schmög et al. with a 83% yield and a 95% conversion of limonene [20]. Menthane was
also synthetized over \( \text{Ni}/\gamma-\text{Al}_2\text{O}_3 \) at 120°C [21]. Nickel loading
of 21%, calcination temperature of 550–650°C, and hydrogen
reduction temperature of 325–350°C were the optimum
conditions for this gaseous phase hydrogenation. Over
hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium
(II) complex immobilized on amine functionalized MCM-41
and SBA-15, menthane was obtained by Joseph et al. at 60°C
and 2.758 MPa of hydrogen pressure in acetonitrile [22].

Over catalyst prepared from RhCl\(_3\) and triphenylphos-
ephine meta-trisulfonate in water, Larpent et al. achieved a
76% conversion of limonene into menthane [23]. In high-
pressure CO\(_2\) and over catalysts containing Pt and Pd [24],
Bogel-Lukasik et al. also converted quantitatively limonene
into menthane at 50°C under 4 MPa of hydrogen pressure
[25]. Partial hydrogenation of limonene to menthene tends to
be problematic due to overreduction. Limonene hydrogena-
tion using Wilkinson’s catalyst confirmed that the hy-
drogenation of the endocyclic double bond is disfavored [26].
Following hydrogenation of limonene over Pd/C and Pd/
Alumina catalysts at room temperature and 0.1 MPa of hy-
drogen pressure, side products, such as terpinolene, g-ter-
pinene, and p-cymene, were formed besides menthene and
menthane [27]. Partial hydrogenation of limonene to men-
there, at low pressure, over Pt on Darco G-60 catalyst was
reported by William [28]. Under mild conditions (room
temperature and low pressure (0.3 MPa), Rubulotta et al.
compared Pd, Ru, and Pt over charcoal and alumina for
limonene’s partial hydrogenation. Over Pt/Alumina, menthe-
ne was obtained with excellent selectivity (90%) and
quantitative limonene’s conversion after 5 h. Under contin-
uous flow conditions, Pt/C provided menthene (87%) with a
conversion of 96% [29]. While dehydrogenation can occur
simultaneously on limonene carbonic cycle to generate
cymene, there is no mention of the percentage of cymene
detected in the previous two studies which ultimately will
contaminate the menthene or the menthane formed.

In recent years, the role of water has received increasing
attention, not only because of its presence in many chemical
reactions, whether as a solvent or as an impurity (trace of
moisture), but also because of its promotional or inhibiting
effect of several transformations [30, 31]. To the best of our
knowledge and of the current literature, the hydrogenation
of limonene over the commonly used catalysts, to obtain
menthene or menthane, in the presence of water has never
been investigated yet. On catalyst’s surface molecular water,
water clusters and dissociated products of water were de-
tected using scanning tunneling microscopy [32–35]. The
presence of water can be the source of hydrogen-bonded
complexes as water is both a hydrogen bond donor and
acceptor, which can accelerate hydrogen transfer and dif-
fusion to promote subsequent hydrogenation or dehydro-
genation [36]. Addition of small amounts of water in
heterogeneous catalysis of natural products appears to im-
prove selectivity and activate the catalyst as demonstrated by
Yamaguchi et al. for the direct production of sugar alcohols
from wood chips using supported platinum catalysts and
also by Tike et al. for the hydrogenation of palm stearin fatty
carbonic acid over ruthenium supported on alumina [37–39].

In this study, supported noble metals including Pd, Pt, Ru,
and Rh, but also some less expensive and therefore more
available metals such as nickel (Ni) and copper (Cu), were
compared for partial and total hydrogenation of limonene. All
hydrogenations were carried out at room temperature and
low and high hydrogen pressure (0.275 MPa and 2.75 MPa).
Conversion yield, dehydrogenation rate selectivity, and the
influence of the catalyst support (carbon, alumina, and silica)
as well as the presence of water in the reaction medium were
investigated. Our hydrogenation experiments were also
designed to investigate the hydrogenation of cymene, a
contaminant for menthene and menthane but yet another
added-value product, on the same catalysts.

2. Materials and Methods

Safety Warning. High-pressure experiments with com-
pressed \( \text{H}_2 \) (g) must be carried out only with appropriate
equipment and under rigorous safety precautions.

2.1. General Experimental Conditions. Limonene and p-
cymene were purchased from Aldrich. 10 wt.% Pd/C
10 wt.% Pd/Alumina, 5 wt.% Pt/C, 5 wt.% Pt/Alumina,
1 wt.% Pt/Silica; 5 wt.% Ru/C, 5 wt.% Ru/Alumina; 5 wt.
% Rh/C, 5 wt.% Rh/Alumina, 3 wt.% Cu/C, and 65 wt.% Ni/
Silica-Alumina were purchased from Aldrich. Pd/Silica
“ISiliaCat Pd(0)” was purchased from Silicycle Inc. \( \text{H}_2 \) (purity
≥99.9%) was purchased from Praxair Canada Inc. NMR
spectra were recorded on Bruker Avance III 400 MHz
spectrometer. GC/MS analysis was recorded on an Agilent
6890 Series GC System coupled to an Agilent 5973 Network
Mass Selective Detector and capillary column (Zebron ZB-
5MS, 30 m × 0.25 mm × 0.25 μm).

GC-MS analysis was recorded on an Agilent 6890 Series
GC System coupled to an Agilent 5973 Network mass
selective detector and capillary column (Zebron ZB-5MS, 30 m × 0.25 mm × 0.25 µm). Instrumentation settings for GC-MS analysis were as follows: samples were prepared with 15 µL of hexane and 10 µL of hydrogenated product. GC inlet was used in splitless mode at 280 °C. Ultrapure helium (Praxair grade 5.0) served as carrier gas at a constant flow rate of 0.8 mL/min. MS transfer line was set at 280°C. MS source was held at 230°C while MS quad was set at 150°C. MS performed scans from m/z 40–400. Ionization technique used was electron impact (EI). Automatic tune setting was used for the MS and tuning was performed before each sequence. GC was initially set at 40°C, held for 0.5 min, then temperature was ramped at 2°C/min to 85°C, and then ramped 40°C/min to 300°C (total run time of 28.38 min). Ten microliters of each sample were diluted in 15 mL hexane (Omnisolve grade from EMD Millipore) and 1 µL of this solution was injected onto the GC-MS for analysis. Dodecanewas tested as external and internal standard. From the total ion chromatogram (TIC) of pure standards of limonene, cymene, menthene, we have identified the retention time and the more appropriate m/z ratio for each compound: m/z of 136 at a retention time of 13.19 min was selected for limonene, m/z of 134 at a retention time of 12.94 min was selected for cymene, m/z of 138 at a retention time of 10.72 min was selected for menthene, m/z of 140 at a retention time of 10.20 min was selected for cis-menthene, and m/z of 140 at a retention time of 10.95 min was selected for trans-menthene. For each sample, the previous m/z ratios were extracted from the TIC to obtain the extracted ion chromatogram (EIC) and the corresponding peak area used for calculation.

All catalyst loadings specified by the commercial supplier were measured for verification by ICP/MS (see supplementary materials, Table S1). For each catalyst, 10 mg was digested using 15 mL of aqua regia (7:3 v/v HCl/HNO3, Trace metal grade, Fisher Scientific). Samples were heated at 75°C for 16 hours using a hot water bath. Catalyst digest samples were further diluted by a factor of 10. Solubilization by 2.3.2. Experimental Solubilization Assay. Solubilization by bead milling was performed using Precellys 24 (Bertin Technology, Ozyme) operating in a 2 mL tube with 1 g of N₂ adsorption-desorption isotherms and BET surface area were collected using a surface area and pore size analyzer (Quantachrome Autosorb-1 MP). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) equipped with an Oxford Inca x-stream EDS system (Oxford Instruments, High Wycombe). Images were collected using an accelerating voltage of 1.5 kV, while EDS spectra were collected at 15 kV. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-1230 operating at 60–120 kV. The H₂ chemisorption was determined via using a RXM-100 analyzer (ASDI) at 40°C.

2.2. Hydrogenation of Limonene and Cymene. 2.5 g of limonene (18.3 mmol) or 2.5 g of p-cymene (18.6 mmol) and a catalyst (Pd/C (10% wt, 0.25 g, 0.23 mmol, 0.01 eq), Pd/C (10% wt, 0.125 g, 0.12 mmol, 0.006 eq), Pd/C (5% wt, 0.25 g, 0.12 mmol, 0.006 eq), Pd/Al₂O₃ (10% wt, 0.234 mmol, 0.006 eq), Pd/Al₂O₃ (10% wt, 0.125 g, 0.12 mmol, 0.006 eq), Pd/Al₂O₃ (10% wt, 0.22 mmol/g, 0.25 g, 0.05 mmol, 0.003 eq), Pt/C (5% wt, 0.5 g, 0.13 mmol, 0.006 eq), Pt/C (5% wt, 0.25 g, 0.03 mmol, 0.004 eq), Pt/Al₂O₃ (5% wt, 0.5 g, 0.13 mmol, 0.006 eq), Pt/Al₂O₃ (5% wt, 0.05 g, 0.03 mmol, 0.004 eq), Ru/C (5% wt, 0.12 mmol, 0.006 eq), Ru/Al₂O₃ (5% wt, 0.12 mmol, 0.006 eq), Rh/C (5% wt, 0.12 mmol, 0.006 eq), Rh/C (5% wt, 0.12 mmol, 0.006 eq), or Rh/Al₂O₃ (5% wt, 0.12 mmol, 0.006 eq)) were added in a 45 mL in-house engineered stainless steel high-pressure autoclave equipped with a glass liner containing a stirring bar. The autoclave was purged four times with hydrogen (1.37 MPa) and then pressurized to 0.275 MPa or 2.75 MPa. Catalysts were not subjected to any treatment prior to hydrogenation. The reaction was stopped after no more change was monitored by GC/MS in the mixture percentage. Hydrogen was vented from the autoclave, and the reaction mixture was filtered through a celite pad to obtain the hydrogenated products. The disappearance of the vinlylic or aromatic protons was confirmed by NMR. The final composition of the mixture was confirmed by GC/MS. Only menthene, menthane, and cymene were detected in our hydrogenation.

2.3. Solubilization of Natural Products

2.3.1. Computational Solubilization Prediction. Solubility abilities of cis-pinane, trans-pinane, cis-rich pinane (cis/trans: 7/3), and n-hexane to dissolve β-carotene, vanillin, and rosmarinic acid were investigated using CONductor-like Screening MOdel for Real Solvents (COSMO-RS) software. The results were expressed in log 10(x-solub) (best solubility is set to 0). The chemical structures of the solvents and solutes discussed in this article were mutually transformed by JChemPaint version 3.3 (GitHub Pages, San Francisco, CA, USA) to their simplified molecular input line entry syntax (SMILES) notations, which were subsequently used to calculate the solubility parameters.

2.3.2. Experimental Solubilization Assay. Solubilization by bead milling was performed using Precellys 24 (Bertin Technology, Ozyme) operating in a 2 mL tube with 1 g of
ceramic beads. 100 mg of compound was mixed with 1 mL of solvent and submitted in drive tube operating at 6500 rpm during 2 * 20 sec. After extraction, the beads were filtered before solid/liquid separation by centrifugation. The samples were stored at −20°C until analysis. All experiments were carried out in triplicates. The total content of each compound was measured spectrophotometrically (Biochrom Libra S22 UV/Vis Spectrophotometer) in a 1 cm optical path-length quartz cell at the maximum wavelength of each compound in each extract using DMSO as a blank. The Beer–Lambert law was used to determine the carotenoid, vanillin, and rosmarinic acid concentration in each extract using a calibration curve prepared using β-carotene, vanillin, and rosmarinic acid standard. The straight calibration curve of absorbance versus compound concentration (mg·L⁻¹) was reliant on the Beer–Lambert law. Finally, the quantity of compound dissolved in each solvent was calculated and expressed as mg·L⁻¹.

3. Results and Discussion

3.1. Hydrogenation over Pd. Palladium over carbon (Pd/C), one of the most used catalysts for hydrogenation, at high pressure converted limonene to the two menthane’s isomers cis (19%) and trans (81%) exclusively with a large amount of cymene, which is due to the dehydrogenation of limonene (Table 1). If the addition of a small amount of water (100 µL) had no effect on the limonene hydrogenation selectivity, it led to a significant decrease of cymene proportion and an increase of menthane. However, hydrogenation in the presence of a greater quantity of water (5 mL) inverted the reaction selectivity: 1-menthene became the major product (78%) while a significant amount of cymene was still formed (53%) [40].

At high pressure and in the absence solvent, Pd/Al₂O₃ was less selective toward the menthane since 71% of menthene was obtained. The addition of a large amount of water provided only menthene with no trace of methene and 28% of cymene. Pd/Silica was selective for the hydrogenation of limonene to menthene. The proportion of menthene dropped considerably following the addition of a small amount of water since only 39% of menthene was obtained. The addition of more water completely deactivated this catalyst, the limonene was not hydrogenated, and no trace of cymene was detected.

At low pressure, the hydrogenation over palladium supported by the three supports was more favorable to the formation of the product of the partial hydrogenation with a longer reaction time in general. The addition of water, especially a large amount, increased the selectivity towards menthene but reduced the conversion rate of limonene to 85% with Pd/Al₂O₃ and Pd/Silica. Even if the low-pressure hydrogenation with Pd/Alumina leads to menthene, the latter was completely hydrogenated after 6 hours of reaction. On the other hand, the presence of water seemed to prevent this double hydrogenation because even after 24 h, menthene was not the major product.

3.2. Hydrogenation over Pt. Compared to Pd/C, Pt/C was very selective for the formation of menthane with no trace of cymene and a very fast hydrogenation (t ≤ 4 h). However, cis-menthane formation was favored since its proportion increased up to 44%.

The addition of water, even in large quantities, had no effect on reactivity as well as selectivity since only menthene was obtained. Compared to Pd/Al₂O₃, Pt/Al₂O₃ was more selective towards the formation of menthene. The addition of a small amount of water increased this selectivity since only menthene was produced with no trace of cymene in only two hours of reaction. The addition of a large amount of water slowed the reaction with a slight decrease in the conversion and no effect on the selectivity. Like Pd/Silica, Pt/Silica also favored menthene formation, but the addition of water, even in large quantities, did not impair its reactivity (Table 2). Similar to Pd, at low pressure, a partial hydrogenation of limonene was achieved on Pt over the three tested supports. Without water, Pt/Silica was the most selective toward menthene since limonene was converted to menthene with 93% of selectivity. Pt/C and Pt/Al₂O₃ lead, respectively, to 66 and 67% of menthene. On the other hand, the menthene obtained from the hydrogenation with Pt/Al₂O₃ was completely transformed into methene after 6 hours of reaction. The addition of a small amount of water was the most efficient in the hydrogenation over Pt/Al₂O₃ since this addition increased the reactivity and the percentage of menthene by 28%. Even if the addition of a greater amount of water led exclusively to menthene, the activity of this catalyst is considerably reduced, especially for Pt/Si, with a conversion yield of less than 3%. At high pressure, no trace of cymene was detected.

3.3. Hydrogenation over Ru. Ru/C was much less effective than Pd/C and Pt/C for the partial or even total hydrogenation of limonene. No conversion of limonene was detected even after 24 hours of reaction. Adding a large amount of water only led to a 7% conversion of limonene. At low pressure, Ru/C was completely inactive without and with the addition of water. Ru/Al₂O₃ was more active than Ru/C, and limonene was converted to menthene (87%) after 24 h of reaction. Catalyst support is therefore of prime importance for its activity. The addition of water reduced the selectivity and the reactivity since only 50% of limonene was hydrogenated in 24 h to menthene in presence of 5 mL of water. At low pressure, both Ru-based catalysts were completely inactive. Only 5% of limonene was converted to menthene with Ru/Al₂O₃ in 24 h. The addition of water had no effect on these two catalysts. Whether at high or low pressures, no trace of cymene was detected (Table 3).

3.4. Hydrogenation over Rh. At high pressure, limonene was completely hydrogenated in menthene over Rh/C in 2 hours. Only 4% of cymene was detected at the end of the reaction. The addition of water decreased the reducing capacity of this catalyst since 79% of menthene was obtained when the hydrogenation was conducted in the presence of a large amount of water. Compared to Pd/Al₂O₃ and Pt/Al₂O₃, Rh/Al₂O₃ was the most selective of the three catalysts for the hydrogenation of limonene to menthene with an equal
proportion of both cis- and trans-isomer. Pt/Al₂O₃ and Pd/Al₂O₃ provide only 4% and 29% of menthane, respectively. Unlike Pd and Pt, the addition of a small amount of water almost completely reversed the selectivity of Rh/Al₂O₃ since menthene is the major product (90%) with no trace of cymene. Hydrogenation in the presence of a greater amount of water increases the selectivity towards menthene to 100% but with a reduced limonene’s conversion (70%). At low pressure, the Rh/C allowed partial hydrogenation of limonene to menthene (88%) in addition to traces of cymene. Adding a small amount of water decreased the selectivity to 66%. On the other hand, the hydrogenation in the presence of a greater quantity of water restored the selectivity to menthene but considerably reduced the reactivity of the catalyst since only 65% of the limonene was hydrogenated after 24 h of reaction (Table 4).

At low pressure, limonene was hydrogenated to menthene with Rh/Al₂O₃ in 3 hours. BZ+he selectivity of this catalyst was clearly pressure-dependent. At high pressure, menthane was exclusively obtained with no traces of cymene. Menthene was solely obtained at reduced pressure with only 5% of cymene. Compared to Rh/C, the Rh/Alumina selectivity’s enhancement could be explained by mechanisms involving Lewis acid sites provided by alumina.

### Table 1: Hydrogenation of limonene over Pd.

| Pressure (MPa) | Support | H₂O | Conversion (%) | Menthene/menthane (%) | Cis/trans menthane (%) | Time (h) | TOF (h⁻¹) | Cymene (%) |
|---------------|---------|-----|----------------|-----------------------|-----------------------|---------|-----------|-----------|
| 2.75          | Carbonᵦ | 100 μL | 100 | 0/100         | 19/81                 | 2       | 39        | 61        |
|               | Al₂O₃ᵦ | 100 μL | 100 | 0/100         | 26/74                 | 2       | 39        | 40        |
|               | —       | 5 mL   | 100 | 78/21        | 20/80                 | 4       | 18.5      | 53        |
|               | 2.75    | Al₂O₃ᵦ | 100 μL | 100 | 71/29        | 29/71                 | 2       | 39        | 28        |
|               | —       | 5 mL   | 100 | 69/31        | 33/67                 | 2       | 39        | 15        |
|               | —       | 5 mL   | 100 | 100/0        | —                     | 6       | 12        | 28        |
|               | —       | 5 mL   | 100 | 39/61        | 27/73                 | 2       | 39        | 0         |
|               | Silicaᵦ | 100 μL | 100 | 0            | —                     | —       | —         | —         |
|               | 0.275   | Carbonᵦ | 100 μL | 100 | 93/7        | 37/63                 | 4       | 19.5      | 7         |
|               | Al₂O₃ᵦ | 100 μL | 100 | 67/33        | 25/75                 | 2       | 39        | 23        |
|               | —       | 5 mL   | 100 | 100/0        | —                     | 24      | 3.2       | 12        |
|               | —       | 100    | 78/18 | 37/63       | 2         | 39        | 4         |
|               | 0.275   | Al₂O₃ᵦ | 100 μL | 100 | 91/9        | 40/60                 | 24      | 2.7        | 44        |
|               | —       | 5 mL   | 85   | 98/2       | 41/59                 | 24      | 2.7        | 44        |
|               | —       | 100    | 96/4  | 43/57      | 6         | 13        | 2         |
|               | —       | 5 mL   | 86   | 98/2       | 20/80                 | 4       | 19.5      | 2         |
|               | Silicaᵦ | 100 μL | 100 | 0            | 100/0                 | 24      | 2.8       | 28        |

### Table 2: Hydrogenation of limonene over Pt.

| Pressure (MPa) | Support | H₂O | Conversion (%) | Menthene/menthane (%) | Cis/trans menthane (%) | Time (h) | TOF (h⁻¹) | Cymene (%) |
|---------------|---------|-----|----------------|-----------------------|-----------------------|---------|-----------|-----------|
| 2.75          | Carbonᵦ | 100 μL | 100 | 0/100         | 37/63                 | 2       | 143       | 0         |
|               | Al₂O₃ᵦ | 100 μL | 100 | 0/100         | 45/55                 | 4       | 71.5      | 0         |
|               | —       | 5 mL   | 100 | 0/100         | 36/64                 | 3       | 95.3      | 0         |
|               | —       | 100    | 96/4  | 48/52      | 2        | 143       | 0         |
|               | —       | 100    | 98/2  | 39/61      | 2        | 143       | 0         |
|               | —       | 5 mL   | 86   | 100/0      | 49/51                 | 4       | 71.5      | 0         |
|               | Silicaᵦ | 100 μL | 100 | 97/3        | 31/69                 | 2       | 143       | 0         |
|               | 0.275   | Carbonᵦ | 100 μL | 100 | 67/33        | 36/64                 | 24      | 12        | 0         |
|               | Al₂O₃ᵦ | 100 μL | 100 | 70/30        | 43/57                 | 6       | 48        | 0         |
|               | —       | 5 mL   | 61   | 100/0        | 6        | 29        | 0         |
|               | —       | 100    | 66/7  | 49/51      | 2        | 104       | 0         |
|               | —       | 5 mL   | 55   | 94/6       | 41/59                 | 6       | 48        | 0         |
|               | —       | 5 mL   | 100  | 93/7       | 45/55                 | 4       | 71.5      | 0         |
|               | —       | 5 mL   | 85   | 98/2       | 47/53                 | 6       | 48        | 0         |
|               | —       | 5 mL   | 3    | 100/0      | 47/53                 | 24      | 3.5       | 0         |

Experimental conditions: pure limonene, the catalyst, and room temperature. *Turnover frequency (TOF) = number of moles of consumed limonene/(mole of catalyst) time of reaction; b5% wt; c0.2 mmol/g.
Lewis acidity of alumina support play an important role in many reactions, including hydrogenation [41, 42]. To detect Brønsted acidity of any dissolved material, pH measurement was carried out. Both the aluminas support and the Rh/Al₂O₃ have rather a neutral Brønsted–Lowry acid character since the measured pH was always in the neutral zone (pH=7.5–8.1). BZ+he addition of a small amount of water slightly reduced the reactivity without affecting the selectivity. However, the addition of more water significantly reduced the reactivity and selectivity while generating a greater amount of cymene.

3.5. Hydrogenation over Ni and Cu. All of our attempts to hydrogenate limonene over Cu/C catalyst failed: the addition of water as well as hydrogenation tests at 100°C, with or without water, did not lead to any hydrogenation or dehydrogenation products. Over Ni/Silica-Alumina, it was possible to hydrogenate 95% of limonene in menthene (63%) and menthane (32%) at high pressure, 100°C, and in the presence of a small amount of water in 24h of reaction. Adding more water greatly reduced the reducing capacity since only 30% of limonene was hydrogenated to menthene only. At low pressure, Ni/Silica-Alumina reduction capacity decreased even further as 46% and 20% of the limonene was converted to menthene in the presence of a small and a large amount of water, respectively.

3.6. Catalyst Comparison. With the second higher TOF (75 h⁻¹), Rh/C is a good catalyst for the conversion of limonene to menthane. This total hydrogenation of limonene was done in 2 h with 4% of cymene formed (Table 4). Larger pore volume, higher surface area, and nanoparticle size (Nps) of Rh/C (pore volume: 0.7 cm³/g, surface area: 815 m²/g, and Nps: 0.93 nm) might explain this higher activity when compared to Rh/Al₂O₃ (pore volume: 0.4 cm³/g, surface area: 150 m²/g, and Nps: 0.76 nm).

Like all the other catalysts tested, the two isomers of menthane (cis- and trans-menthane) were obtained with variable proportions but with a slight preference for the trans isomer. At high pressure and in the presence of a small amount of water, Rh/Al₂O₃ was the most powerful catalyst (TOF = 151 h⁻¹) for converting limonene mainly to menthene in just 2h.

Although it has a larger measured surface area than Rh/Al₂O₃ (150 m²/g), Rh/C (815 m²/g) performs less than Rh/Al₂O₃ in the presence of water for synthesis of the partial...
hydrogenation product. Measured pore diameter difference (Rh/Al2O3: 74.4 Åo, Rh/C: 10.8 Åo) may explain this performance disparity. Additionally, from SEM images (see supplementary materials, Figures S1 and S2), it can be observed that the particles of Rh/C were agglomerated/sintered which could explain its weaker activity compared to Rh/Al2O3. Over alumina, Rh had a larger catalytic surface area (150 m²/g) and a larger nanoparticles size (Nps 16 nm) than those of Pt and Ru [29, 43].

A larger promoter effect of water combined with the large difference in size of Rh nanoparticles on these two supports might explain this difference.

Rh/Alumina which was never tested for total and partial hydrogenation of limonene was the most effective as menthene was quantitatively produced at low pressure (0.275 MPa) while menthane was mostly obtained at a higher pressure (2.75 MPa). Water addition on Rh/Alumina favoured menthene production even at high pressure (Table 4).

Alumina Lewis acidic character as well as water effect can explain these results. More tests, in particular on catalysts after hydrogenation, will be necessary to elucidate the water-catalyst interactions.

Investigation of limonene’s hydrogenation with the selected catalysts revealed that limonene’s partial hydrogenation is pressure-dependent. At low pressure, all catalysts, except Ru, independent of the supports were menthene selective. It was reported that hydrogenation of the limonene’s endocyclic double bond was disfavored compared to the exocyclic double bond’s hydrogenation [26]. It was also reported that Ru/C has smallest nanoparticles (1.5 nm), compared to the other investigated metals, which could explain its inactivity on our hydrogenation [29].

3.7. Rh/Al2O3 Recycling and Kinetic Studies. Based on our results, we selected Rh/Al2O3 for further recycling tests and kinetic studies. Rh/Alumina was the best switchable catalyst with a higher selectivity toward 1-menthene in the presence of a small amount of water. The same catalyst, without the addition of water, led exclusively to menthane with no traces of cymene. To the best of our knowledge, this catalyst has never been tested for the solvent-free hydrogenation of limonene and the effect of pressure and water addition on the selectivity has never been investigated. The absence of cymene during the hydrogenation of limonene with this catalyst compared to the most common catalysts used for hydrogenation has never been investigated as well.

At high pressure and after one hour of reaction over Rh/Alumina, all limonene was converted into a mixture of menthene and menthane (1:1). During the remaining 5 hours of reaction, menthene was gradually converted into menthane (Figure 1).

At high pressure and in the presence of water, after about one hour of hydrogenation over Rh/Alumina, limonene was also almost completely converted into menthene (Figure 2). Menthane began to be produced in small proportion after 30 minutes of reaction. Hydrogenation of limonene remained therefore partial since the proportion of menthene continued to increase between 30 and 40 minutes of hydrogenation.

The low proportion of the menthane formed after 45 minutes of reaction could also be attributed to menthene’s own hydrogenation: a 10% proportion of menthane was achieved once limonene was completely converted and remained unchanged even after several hours of reaction.

The potential to recycle Rh/Alumina was tested by repeatedly adding fresh limonene into the reactor vessel once the hydrogenation of each cycle was complete. In presence of 100 µL of water, Rh/Alumina was reused successfully 7 times with no decline in activity (Table 5).

Without addition of water, Rh/Al2O3 provided menthane (44/56 cis/trans) exclusively in the first cycle, but becomes highly selective towards menthene from the second cycle: limonene’s hydrogenation over the recycled catalyst lead after 2 h to a complete conversion of limonene into 85% of menthene and only 15% of menthane.
The menthene selectivity increased significantly from 85% to 97% after the third run (Table 5). This decrease in the strength of this catalyst, even in the absence of water, can be exploited perfectly for the production of menthene. After reducing its strength, with a first hydrogenation, Rh/Al₂O₃ was filtered after half-time reaction, the hydrogenation of the generated cymene. It is the main reason that why cymene hydrogenation was investigated due to either the non-dehydrogenation of the limonene or to the hydrogenation of the generated cymene. It is the main reason that why cymene hydrogenation was investigated with all tested catalysts in this study. Cymene hydrogenation over only Pd/C has been investigated by Stalzer et al. for comparison with the single-face arene hydrogenation by a supported organozirconium catalyst [44].

With Pd, only Pd/C allows a very slow hydrogenation of cymene to menthene. No conversion to menthane was observed over Rh/Al₂O₃ or Pd/Silica even after 24h of reaction, which confirmed the lack of Rh catalyst in the filtrate and the heterogeneous catalytic nature of the reaction. To confirm the heterogeneous nature of the catalysis, Rh leached from the Rh/Alumina catalyst into the menthene or menthane solution was measured by ICP/MS: it never exceeded 0.002% of the initial Rh amount. When Rh/Al₂O₃ was filtered after half-time reaction, the hydrogenation of the filtrate without the filtered catalyst, at the same hydrogen pressure and temperature, failed even after 24 h of reaction, which confirmed the lack of Rh catalyst in the filtrate and the heterogeneous catalytic nature of the reaction.

3.9. Solubilization Assays. Menthene and menthane, obtained from limonene, were tested as a bio-based alternative solvent for the solubilization of various natural products such as carotenoids, vanillin, and rosmarinic acid. As predicted by COSMO-RS, menthene and menthane showed high probability of solubility of β-carotene and vanillin rather than rosmarinic acid.

Experimentally, the solubility of β-carotene, vanillin, and rosmarinic acid in obtained menthene and menthane as solvents was investigated by bead milling. Menthene appeared to be the best solvent; it solubilized β-carotene, vanillin, and rosmarinic acid three to five times better than n-hexane (Table 7). Menthene as well as menthane showed high probability of solubility of β-carotene and vanillin rather than rosmarinic acid.
menthene solubilized three and five times better than menthane. The mixture becomes equivalent to hexane for menthane. 

At high pressure and with the same catalyst but in the presence of a small amount of water, there is a reversal of the selectivity since menthene became the major product. The addition of water reverses only the selectivity in the hydrogenation of limonene over Rh, since this inversion is not observed with the other tested catalysts. This inversion is much more important over Rh/Alumina than with Rh/C. 

At low pressures, the conversion of limonene was either not complete or the selectivity did not reach 90% in menthene and the reaction was too slow. In terms of recyclability, Rh/Alumina, with the addition of water, was recycled 7 times with no decline in selectivity and activity. The same catalyst, after the first run, was recycled 5 times with no decline in selectivity and activity. Rh has been found to be the best catalyst for cymene’s hydrogenation compared to the six tested metals. Over Rh/C or Rh/Alumina, cymene was efficiently converted into menthene exclusively in only one hour. Rh/C and Rh/Alumina were recycled 6 and 5 times, respectively, with no decline in activity.

Compared to n-hexane, menthene solubilized more β-carotene, vanillin, and rosmarinic acid. Consequently, menthene, as well as menthene containing menthene, could be interesting bio-based solvents to replace fossil-based solvents such as n-hexane for the extraction of several natural products widely used in many industries.

Table 7: COSMO-RS relative solubility (log10(x-solub)) of β-carotenoids, vanillin, and rosmarinic acid in n-hexane, menthene, and menthane.

| Compounds         | n-Hexane (log10(x-solub)) | Menthene (log10(x-solub)) | Menthane (log10(x-solub)) |
|-------------------|---------------------------|---------------------------|---------------------------|
| β-Carotene        | −0.0087                   | 0.0                       | 0.0                       |
| Vanillin          | −2.499                    | −2.129                    | −2.516                    |
| Rosmarinic acid   | −9.099                    | −8.083                    | −9.140                    |

Table 8: β-Carotene, vanillin, and rosmarinic acid solubility in n-hexane, menthene, and menthane.

| Solvent                  | β-Carotene solubility (mg·mL⁻¹) | Vanillin solubility (mg·mL⁻¹) | Rosmarinic acid solubility (mg·mL⁻¹) |
|--------------------------|---------------------------------|-------------------------------|-------------------------------------|
| n-hexane                 | 0.99 ± 0.06                     | 1.19 ± 0.09                   | 0.54 ± 0.01                         |
| Menthene/menthane (90/10)| 3.55 ± 0.10                     | 6.07 ± 0.24                   | 2.11 ± 0.18                         |
| Pure menthene            | 2.85 ± 0.14                     | 1.03 ± 0.14                   | 0.33 ± 0.04                         |
| Menthene/menthane (98/2) | 3.53 ± 0.18                     | 6.95 ± 0.18                   | 0.65 ± 0.04                         |

4. Conclusion

Partial and total solvent-free hydrogenation of limonene was investigated using commercially available catalysts under high and low hydrogen pressure with or without water. Compared to palladium, ruthenium, platinum, nickel, and copper, Rh was an excellent catalyst for the hydrogenation of limonene to menthene and menthane. Over Rh/Alumina, menthene, the product of total hydrogenation, was obtained solely at high pressure with a turnover number around 150.

As presented in Table 8, menthane containing 2% of menthene solubilized three and five times better than n-hexane β-carotene and vanillin, respectively. This same mixture becomes equivalent to n-hexane for the solubilization of rosmarinic acid (Table 8).

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

The authors would like to acknowledge the contribution of the New Brunswick Innovation Foundation (grant no. RIF2015-014 to M.T.) and the Canadian Foundation for Innovation (Leaders Opportunity Fund (grant no. 17996 to M.T.). The authors thank Dr. Y. Djoued, R. Cormier, N. A. Levesque, J. Robichaud, M. Jebali, and A. Landry for their support for the catalyst characterizations. The authors also thank Dr. A. Nait Ajjou for sharing his autoclave and Dr. Simon Lamarre for sharing his GC-MS.

Supplementary Materials

Table S1: catalyst loadings measured by ICP/MS. Table S2: Rh-based catalyst features. Figure 2S: Rh/Alumina particle size distribution measured by TEM. Figure 1S: Rh/C particle size distribution measured by TEM. (Supplementary Materials)

References

[1] S. Tanielyan, N. Biunno, R. Bhagat, and R. Augustine, "Anchored Wilkinson catalyst: hydrogenation of β-pinene," Topics in Catalysis, vol. 57, no. 17–20, pp. 1564–1569, 2014.
[2] M. Aissou, Z. Chemat-Djenni, E. Yara-Varón, A. Fabiano-Tixier, and F. Chemat, "Limonene as an agro-chemical building block for the synthesis and extraction of bioactive compounds," Comptes Rendus Chimie, vol. 11, no. 20, pp. 346–358, 2017.
[3] L. Xie, X. Wang, F. Yu, B. Yuan, C. Xie, and S. Yu, "Preparation of cis-pinane via α-pinene hydrogenation in water by using Ru nanoparticles immobilized in functionalized amphiphilic mesoporous silica," RSC Advances, vol. 7, no. 81, pp. 51452–51459, 2017.
10 Journal of Chemistry

[4] E. Yılmazoğlu and M. Akgün, “p-Cymene production from orange peel oil using some metal catalyst in supercritical alcohols,” *The Journal of Supercritical Fluids*, vol. 131, pp. 37–46, 2018.

[5] H. Cui, J. Zhang, Z. Luo, and C. Zhao, “Mechanisms into dehydroaromatization of bio-derived limonene to p-cymene over Pd/HZSM-5 in the presence and absence of H2,” *RSC Advances*, vol. 6, no. 71, pp. 66695–66704, 2016.

[6] R. Augustine, *Heterogeneous Catalysis for the Synthetic Chemist*, CRC Press, New York, NY, USA, 1996.

[7] F. Zacchera and N. Ravasio, “Catalytic reduction in organic synthesis,” *Science of Synthesis*, vol. 1, p. 111, 2017.

[8] R. Mathers and M. Meier, *Green Polymerization Methods*, Wiley VCH, Weinheim, Germany, 2011.

[9] M. Golets, S. Ajaikumar, and J.-P. Mikkola, “Catalytic upgrading of extractives to chemicals: monoterpenes to “EXICALS”,” *Chemical Reviews*, vol. 115, no. 9, pp. 3141–3169, 2015.

[10] I. Pérez and J. G. Ávila-Zárraga, “Synthesis of puleganic amides via a catalytically efficient two-step approach,” *Tetrahedron Letters*, vol. 59, no. 32, pp. 3077–3079, 2018.

[11] S. Selifonov, “Methods for making (−)-menthol and oxygenated menthane compounds,” US Patent US2003/023120, 2006.

[12] C. Daeppen, M. Kaiser, M. Neuburger, and K. Gademann, “Preparation of antimalarial endoperoxides by a formal [2 + 2 + 2] cycloaddition,” *Organic Letters*, vol. 17, no. 21, pp. 5420–5423, 2015.

[13] S. Schoenauer and P. Schieberle, “Structure-odor activity studies on monoterpenoid mercaptans synthesized by changing the structural motifs of the key food odorant 1-p-Menthene-8-thiol,” *Journal of Agricultural and Food Chemistry*, vol. 64, no. 19, pp. 3849–3861, 2016.

[14] C. Nancy and J. B. Jeffrey, “Modified creping adhesive composition and method of use thereof,” US Patent 7404875B2, 2008.

[15] R. Rios-Estepa, G. W. Turner, J. M. Lee, R. B. Croteau, and B. M. Lange, “A systems biology approach identifies the biochemical mechanisms regulating monoterpenoid essential oil composition in peppermint,” *Proceedings of the National Academy of Sciences*, vol. 105, no. 8, pp. 2818–2823, 2008.

[16] V. K. Bhatia, K. G. Mittal, R. P. Mehrotra, and M. Mehrotra, “Hydrocarbon fuels from biomass,” *Fuel*, vol. 68, no. 4, pp. 475–479, 1989.

[17] N. I. Tracy, D. Chen, D. W. Crunkleton, and G. L. Price, “Hydrogenated monoterpenes as diesel fuel additives,” *Fuel*, vol. 88, no. 11, pp. 2238–2240, 2009.

[18] J. L. Kuester, “Liquid hydrocarbon fuels from biomass,” *ACS Symposium Series*, vol. 144, no. 8, pp. 163–184, 1981.

[19] M. A. Fraga, L. Borges, and F. R. Gonçalves, “Catalytic process of limonene hydrogenation for producing p-Menthane and use of the p-Menthane produced as aviation biofuel,” WO Patent 2012021856 A1, 2012.

[20] C. Schmöger, A. Stolle, W. Bonrath et al., “A practical approach for ambient-pressure hydrogenations using Pd on porous glass,” *ChemSusChem*, vol. 2, no. 1, pp. 77–82, 2009.

[21] C. B. Dai, G. F. Pan, R. D. Li, and H. Wang, “The study on dipentene hydrogenation catalyst,” *Advanced Materials Research*, vol. 550–553, pp. 371–374, 2012.

[22] J. Trissa, S. S. Deshpande, S. B. Halligudi, A. Vinu, S. Ernst, and M. Hartmann, “Hydrogenation of olefins over hydrid chlorocarbonyltris- (triphenylphosphine) ruthenium (II) complex immobilized on functionalized MCM-41 and SBA-15,” *Journal of Molecular Catalysis A: Chemical*, vol. 206, no. 1-2, pp. 13–21, 2003.

[23] L. Chantal, D. René, and P. Henri, “Catalytic hydrogenation of olefins in biphasic water-liquid system,” *Tetrahedron Letters*, vol. 28, no. 22, pp. 2507–2510, 1987.

[24] E. Bogel-Lukasik, I. Fonseca, R. Bogel-Lukasik et al., “Phase equilibrium-driven selective hydrogenation of limonene in high-pressure carbon dioxide,” *Green Chemistry*, vol. 9, no. 5, pp. 427–430, 2007.

[25] E. Bogel-Lukasik, R. Bogel-Lukasik, and M. Nunes da Ponte, “Effect of flow rate of a biphasic reaction mixture on limonene hydrogenation in high pressure CO2,” *Industrial & Engineering Chemistry Research*, vol. 48, no. 15, pp. 7060–7064, 2009.

[26] S. K. Tanielyan, R. L. Augustine, N. Marin, and G. Alvez, “Anchored Wilkinson catalyst,” *ACS Catalysis*, vol. 1, no. 2, pp. 159–169, 2011.

[27] J. G. Ricardo, D. Z. Patricia, G. Carolina, and A. T. Hugo, “Liquid phase hydrogenation, isomerization and dehydrogenation of limonene and derivatives with supported palladium catalysts,” *Journal of Molecular Catalysis A: Chemical*, vol. 148, no. 1-2, pp. 203–221, 1999.

[28] F. N. William, “Derivatives of (+)-Limonene. I. Esters of trans-p-Menthene-1,2-diol11,” *Journal of Organic Chemistry*, vol. 23, no. 9, pp. 1274–1276, 1958.

[29] G. Rubulotta, K. L. Luska, C. A. Urbina-Blanco et al., “Highly selective hydrogenation of R-(+)-Limonene to (+)-(−)-p-1-Menthene in batch and continuous flow reactors,” *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 5, pp. 3762–3767, 2017.

[30] C. R. Chang, Y. F. Zhao, B. Long, Z. Q. Huang, and J. Li, “On the catalytic role of water in chemical reactions: an overview,” *Scientia Sinica Chimica*, vol. 46, no. 1, pp. 1–11, 2016.

[31] R. N. Butler and A. G. Coyne, “Water: nature’s reaction enhancer-comparative effects for organic synthesis “in-water” and “On-Water”,” *Chemical Reviews*, vol. 110, no. 10, pp. 6302–6337, 2010.

[32] S. Maier and M. Salmeron, “How does water wet a surface?” *Accounts of Chemical Research*, vol. 48, no. 10, pp. 2783–2790, 2015.

[33] T. K. Shimizu, A. Mugarza, J. I. Cerda et al., “Surface species formed by the adsorption and dissociation of water molecules on a Ru(0001) surface containing a small coverage of carbon atoms studied by scanning tunneling microscopy,” *The Journal of Physical Chemistry C*, vol. 112, no. 19, pp. 7445–7454, 2008.

[34] T. Mitsui, M. K. Rose, E. Fomin et al., “Water diffusion and clustering on Pd(111),” *Science*, vol. 297, no. 5588, pp. 1850–1852, 2002.

[35] S. Maier, I. Stass, J. I. Cerda, and M. Salmeron, “Unveiling the mechanism of water partial dissociation on Ru (0001),” *Physical Review Letters*, vol. 112, no. 12, Article ID 126101, 2014.

[36] R. J. Buszek, J. S. Francisco, and J. M. Anglada, “Water effects on atmospheric reactions,” *International Reviews in Physical Chemistry*, vol. 30, no. 3, pp. 335–369, 2011.

[37] L. Tianxiang, Z. Yongming, Z. Hongxi et al., “Effect of flow rate of a biphasic reaction mixture on limonene hydrogenation in high pressure CO2,” *Industrial & Engineering Chemistry Research*, vol. 48, no. 15, pp. 4845–4849, 2016.

[38] Y. Aritomo, S. Osamu, M. Naoki et al., “Direct production of sugar alcohols from wood chips using supported platinum catalysts in water,” *Catalysis Communications*, vol. 54, pp. 22–26, 2014.

[39] A. T. Manoj and V. M. Vijaykumar, “Kinetics of hydrogenation of palm stearin fatty acid over Ru/Al2O3 catalyst in high-pressure carbon dioxide,” *ChemSusChem*, vol. 2, no. 1, pp. 203–207, 2009.
presence of small quantity of water,” *Indian Journal of Chemical Technology*, vol. 14, no. 1, pp. 52–63, 2007.

[40] T. N. Gieshoff, M. Villa, A. Welther et al., “Iron-catalyzed olefin hydrogenation at 1 bar H₂ with a FeCl₃-LiAlH₄ catalyst,” *Green Chemistry*, vol. 17, no. 3, pp. 1408–1413, 2015.

[41] D. R. Kennedy, G. Webb, S. D. Jackson, and D. Lennon, “Propyne hydrogenation over alumina-supported palladium and platinum catalysts,” *Applied Catalysis A: General*, vol. 259, no. 1, pp. 109–120, 2004.

[42] R. L. Flesner and J. L. Falconer, “The role of spillover in carbon monoxide hydrogenation over alumina-supported platinum,” *Journal of Catalysis*, vol. 139, no. 2, pp. 421–434, 1993.

[43] M. Katarzyna, T. Kin, and E. T. Shik Chi, “Comparison of catalytic performance of supported ruthenium and rhodium for hydrogenation of 9-ethylcarbazole for hydrogen storage applications,” *Energy & Environment Science*, vol. 5, no. 9, p. 8621, 2012.

[44] M. M. Stalzer, C. P. Nicholas, A. Bhattacharyya, A. Motta, M. Delferro, and T. J. Marks, “Single-Face/All-cis arene hydrogenation by a supported single-site d0 organozirconium catalyst,” *Angewandte Chemie International Edition*, vol. 55, no. 17, pp. 5263–5267, 2016.