PRODUCTION OF ISOMALT WITH HYDROGENATION METHOD

Miss Suratsawadee Sukeesan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2012

การผลิตไอโซมอลด้วยกระบวนการไฮโดรจิเนชัน

นางสาวสุรัสวดี สุขีสาร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2555

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Thesis Title	PRODUCTION OF ISOMALT WITH HYDROGENATION METHOD
By	Miss Suratsawadee Sukeesan
Field of Study	Chemical Engineering
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Thesis Co-Advisor	Assistant Professor Worapon Kiatkittipong, D.Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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สุรัสวดี สุขีสาร : การผลิตไอโซมอลด้วยกระบวนการไฮโดรจิเนชัน. (PRODUCTION OF ISOMALT WITH HYDROGENATION METHOD) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร. ประเสริฐ ภวสันต์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร. วรพล เกียรติกิตติพงษ์, 88 หน้า.

งานวิจัยนี้ทำการศึกษาการผลิตไอโซมอลด้วยกระบวนการไฮโดรจิเนชัน โดยมีจุดมุ่งหมายในการหาภาวะที่เหมาะสมในการผลิตไอโซมอลด้วยตัวเร่งปฏิกิริยารูทีเนียมบนถ่านกัมมันต์ ที่สังเคราะห์ขึ้นเอง โดยเตรียมตัวเร่งปฏิกิริยาคือรูทีเนียมบนถ่านกัมมันต์ด้วยวิธีเคลือบฝัง แล้วทำการวิเคราะห์ตัวเร่งปฏิกิริยาโดยเทคนิค BET, XRD และ XRF สำหรับปฏิกิริยาไฮโดรจิเนชันจะทำในเครื่องปฏิกรณ์แบบอัดความดันควบคุมความเร็วรอบของใบกวนที่ 670 รอบต่อนาที โดยสารตั้งต้นในการผลิตไอโซมอลคือไอโซมอลทูโลส 40 เปอร์เซ็นต์โดยน้ำหนัก พบว่าการเตรียมตัวเร่งปฏิกิริยาคือรูทีเนียมบนถ่านกัมมันต์โดยมีรูทีเนียมร้อยละ 10 โดยน้ำหนักแล้วนำไปเผาที่อุณหภูมิ 500 องศาเซลเซียสในแก๊สอาร์กอน และนำไปเผาไล่ไฮโดรเจนที่อุณหภูมิ 200 องศาเซลเซียสในแก๊สไฮโดรเจน เป็นสภาวะการเตรียมที่ดีที่สุด และทำการศึกษาสภาวะการเกิดปฏิกิริยาไฮโดรจิเนชันโดยการเปลี่ยนแปลงปัจจัยที่มีอิทธิพลในการผลิต 4 ปัจจัยคือ ปริมาณรูทีเนียมที่เติมลงบนถ่านกัมมันต์ สัดส่วนของตัวเร่งปฏิกิริยาต่อไอโซมอลทูโลสตั้งต้น ความดัน และ อุณหภูมิ พบว่า รูทีเนียม 10 เปอร์เซ็นต์โดยน้ำหนักของตัวเร่งปฏิกิริยา ที่สัดส่วนของตัวเร่งปฏิกิริยาต่อไอโซมอลทูโลสตั้งต้นที่มีค่าสูงสามารถเพิ่มความว่องไวในการเกิดปฏิกิริยา และสภาวะที่เหมาะสมในการผลิตคือที่อุณหภูมิ 130 องศาเซลเซียส และความดัน 50 บาร์ ซึ่งจากการศึกษาจลนพลศาสตร์ของการเร่งปฏิกิริยาตามแบบจำลองพื้นฐานทฤษฎีของแลงเมียร์-ฮินเชลวูด-ฮอยเกนและวัตสัน พบว่าเป็นปฏิกิริยาอันดับที่หนึ่ง และค่าคงที่ของอัตราการเกิดปฏิกิริยาเป็นไปตามทฤษฎีของอาร์เรเนียสคือค่าคงที่ของปฏิกิริยาจะเพิ่มขึ้นตามอุณหภูมิในการทำปฏิกิริยา จากนั้นทำการศึกษาเสถียรภาพของตัวเร่งปฏิกิริยาพบว่าตัวเร่งปฏิกิริยารูทีเนียมบนถ่านกัมมันต์ที่สังเคราะห์ขึ้นเองนั้นสามารถนำกลับมาใช้ได้ใหม่ได้อีก 2-3 ครั้งโดยยังจะผลิตไอโซมอลได้อย่างสมบูรณ์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

5370515021 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : ISOMALT / SUGAR ALCOHOL / HYDROGENATION / Ru/C CATALYST

SURATSAWADEE SUKEESAN : PRODUCTION OF ISOMALT WITH HYDROGENATION METHOD. ADVISOR : ASSOC. PROF. PRASERT PAVASANT, Ph.D., CO-ADVISOR : ASST. PROF. WORAPON KIATKITTIPONG, D.Eng., 88 pp.

In this research, the effects of operating conditions on the hydrogenation of isomaltulose were evaluated. The reaction was catalyzed with Ru/C catalysts prepared from the impregnation of Ruthenium on activated charcoal powder. The catalysts were characterized by N_2 physisorption, XRD and XRF techniques. The reactions were carried out in a pressure vessel stirring reactor, with isomaltulose (40 wt% in DI water) where the impeller speed was maintained at a maximum speed of 670 rpm. The Ru/C catalyst was calcined in argon at 500°C for 4 h, and reduced at 200°C under flowing H_2 for 2 h. The hydrogenation of isomaltulose was successfully performed with 10% Ru/C catalysts. The rate of reaction increased with increasing weight ratio of catalyst/reactants at the reaction temperature of 130 °C and 50 bar. The reaction rate followed the first order dependency with respect to hydrogen. The kinetics fitted best with Langmuir-Hinshelwood-Hougen-Watson (LHHW). The observed activation energy confirmed that the reaction was under chemical control. The Ru/C catalyst seemed to be relatively stable as it still provided a complete hydrogenation of isomaltulose even after reusing in three consecutive batches.

Department : Chemical Engineering
Field of Study : Chemical Engineering
Academic Year : 2012

Student's Signature
Advisor's Signature
Co-advisor's Signature

ACKNOWLEDGEMENTS

The author would like to express his greatest gratitude and appreciation to his advisor and co-advisor, Associate Professor Dr. Prasert Pavasant and Assistant Professor Dr. Worapon Kiatkittipong for his encouragements, invaluable guidance, providing value suggestions, and his kind supervision throughout this study. In addition, he is also grateful to Associate Professor Dr. Tharathon Mongkhonsi, as the chairman, Associate Professor Dr. Joongjai Panpranot and Associate Professor Dr. Tawan Sooknoi as the committee. I have learned a lot from all of the committee members in many different aspects.

Special thanks are given to Mr.Songphon Phimsen and many friends in Faculty of Engineering and Industrial Technology Silpakorn University, who provided me with many experimental facilities during my research. The author wishes to thank many friends in Biochemical and Environmental Chemical Engineering & Safety Research Laboratory who always provide the encouragement along the thesis study.

This study was financially supported by Rajburi Sugar Co., Ltd, and Special thanks to Evonik Industries AG for providing the commercial Ruthenium catalyst supports throughout my research.

Finally, I would like to dedicate the achievement of this work to my beloved parents and family, who have always been the source of suggestion, support and encouragement.

CONTENTS

Page

Page

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

NOMENCLATURES

$C_{isomalt}$	Isomalt concentration (mol l^{-1})
$C_{Isomaltulose}$	Isomaltulose concentration (mol l^{-1})
$C_{calculated}$	Concentration calculated by the model during parameter estimation (mol l^{-1})
$C_{experimental}$	Experimental concentration (mol l^{-1})
C_{mean}	Mean concentration for all the experimental value(mol l^{-1})
E_a	Activation energy of isomaltulose (kJ mol^{-1})
TOF	Turnover frequency (mol s^{-1} $g_{metal}{}^{-1}$)
k	Rate constant (s^{-1} $g_{metal}{}^{-1}$)
$w_{catalyst}$	The weight of metal in catalyst (g_{metal})
r_i	Rate of reaction (mol l^{-1} s^{-1})
P_{H2}	Hydrogen gas pressure (bar)
K_{H2}	Adsorption constants of hydrogen (bar^{-1})
$K_{isomaltulose}$	Adsorption constants of isomaltulose (l mol^{-1})
ΔH_H	Heat of adsorption of hydrogen (kJ mol^{-1})
$\Delta H_{isomaltulose}$	Heat of adsorption of isomaltulose (kJ mol^{-1})
R^2	Coefficient of determination (%)
A	Exponential factor
T	Temperature (K)
R	Gas constant (8.3145 $mol^{-1}K^{-1}$)

CHAPTER I

INTRODUCTION

1.1 Motivations

Thai people have long been familiar with using sugar as sweet additive in both food and beverage. Nevertheless, the use of sugar as sweeteners may cause problems in the elderly and some group of people with diabetes. In addition, excessive use of sugar can also result in tooth decay. These health problems have induced the country extravagant cost of health care. To alleviate the problems mentioned above, sweetener alternatives with no adverse health effect have been proposed, such as sugar alcohol (polyols) (Cammenga and Zielasko, 1996). Some sugar substitutes could provide lesser sweetness, some provide the same sweetness, or some sweeter than the most commonly used sucrose from sugar cane (Akinterinwa et al., 2008).

Isomalt belongs to sugar alcohol family and has been employed as a sweetener in a similar fashion with sorbitol, mannitol, xylitol, and maltitol (Baek et al., 2004). These are considered low-calorie sweeteners classified to the group of sugar-free. This sugar is a white odorless crystalline substance with low moisture content, and also sweets like candies, wafers, etc. This sugar is considered a natural product, being derived from sugar cane, and it provides sweetness in an equivalent level to sucrose without causing dental problems (Wheeler and Pi-Sunyer, 2008). In addition, compared to sucrose, it provides lesser energy and lower Glycemic Index (GI) which are suitable for pharmaceutical and neutraceutical products (for the elderly and diabetes). The use of sugar of this type would help relieve the symptoms of high blood sugar levels which could help reduce the burden of health care (Bolhuis et al., 2009).

Isomalt can be produced from sucrose by enzymatic conversion of sucrose into isomaltulose and then hydrogenation to isomalt. The transformation of sugar with hydrogenation reaction needs the use of proper catalyst, often Ni based. The active Ru catalyst has been reported to give higher activity than Ni catalyst (Eisenbeis et al., 2009). The hydrogenation of some natural sugars to corresponding sugar alcohols in aqueous solutions was investigated on Ru/C catalysts where the hydrogenation of D-maltose, D-galactose, L-arabinose and L-rhamnose was successfully performed with a Ruthenium supported on activated carbon (Ru/C) catalyst in a pressurized slurry reactor (Sifontes et al., 2011). Such hydrogenation reaction needs to be performed under several control variables including temperature, pressure, type of catalyst, initial sugar concentration and other impurities that could also react with H_2. Lack of literature in this area makes it difficult to assemble and optimize the production system for isomalt.

The objective of this study was to produce isomalt with hydrogenation over Ru/C catalyst and to determine suitable operating conditions for hydrogenation. Several operating parameters along with the setup of the hydrogenation reactor were examined.

1.2 Objectives

1.2.1 To synthesize Ru/C catalysts with the capability to convert isomaltulose to isomalt

1.2.2 To optimize the production of isomalt by hydrogenation of isomaltulose using the synthesized Ru/C catalyst

1.2.3 To determine the kinetic parameters of the hydrogenation of isomaltulose to isomalt.

1.3 Working scopes

1.3.1 The optimization of hydrogenation reaction is performed over the following variables and their associated ranges:

1.3.1.1 Temperature (100,120, 130 °C)

1.3.1.2 Pressure (30,40, 50 bar)

1.3.1.3 Time (1, 2, 3, 4, 5, 6, 7, 8 h)

1.3.1.4 Reuse catalyst (1, 2, 3, 4 time)

1.3.2 The catalysts selected for this process are Ruthenium supported on activated carbon.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

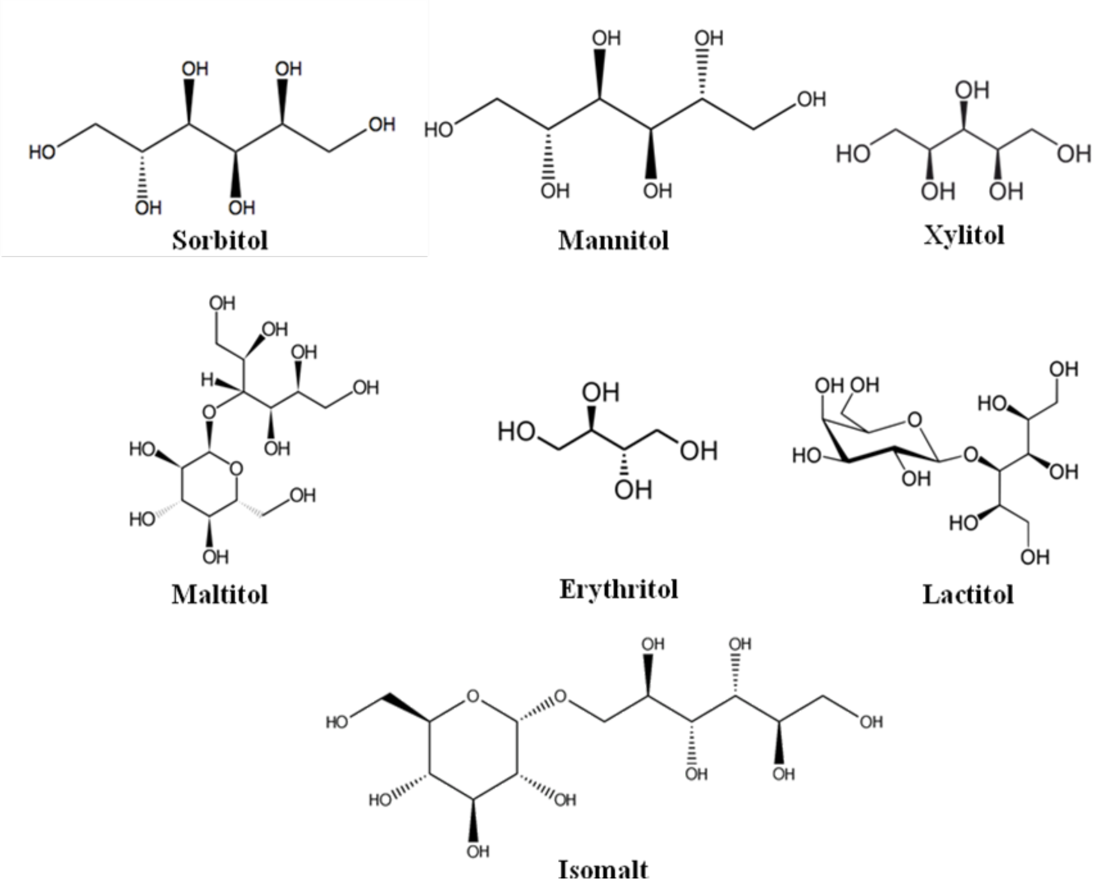
2.1 Sugar alcohol

Today, sugar alcohols (also known as polyols) have become essential ingredients in a wide range of food applications, both of their functional, sensorial as well as nutritional properties. They naturally occur in foods and come from plant products such as fruits and vegetables. These products may assist consumers in maintaining good oral health, maintaining or reducing weight and reducing Glycemic Index (GI) (Livesey, 2003).

2.1.1 General information of sugar alcohol

Sugar alcohols are chemically defined as saccharide derivatives in which a ketone or aldehyde group is replaced by a hydroxyl group (Zumbe et al., 2001). They chemically reduced carbohydrates (slightly less calories than sugar) that provide sweetness to foods. Sugar alcohols derived from the hydrogenation of their sucrose or syrup source. This classification including sorbitol, mannitol, xylitol, isomalt, maltitol, lactitol and erythritol (Bornet, 1994) present in the molecule shows in Figures 2.1.

Sorbitol is commercially produced from glucose, and can be found in numerous berries and higher plants. Maltitol, isomalt and lactitol are disaccharides derived from hydrogenation of maltose isomaltulose and lactose, respectively and being most frequently present in plant exudates. Erythritol exists in fruits such as pears, melons and grapes, as well as foods such as mushrooms and fermentation-derived foods such as wine, soy sauce and cheese. Like xylitol, mannitol is also endogenous metabolites in mammals (Wolever et al., 2002). Table 2.1 shows properties, the sweetness of sugar alcohols compared with sucrose and commonly used sugar alcohols along with some of their food applications. Manufacturers frequently use sugar alcohols in combination with other polyols and with nutritive sweeteners to attain the desired taste and sweetness level (Freeman and Hayes, 2004).



Sorbitol Mannitol Xylitol

Maltitol Erythritol Lactitol

Isomalt

Figure 2.1 Structures of common sugar alcohols

Table 2.1 Properties of sugar alcohol (Milda et al., 2001)

Type of Sugar alcohol	**Calories per gram**	**Approximate Sweetness (sucrose =100%)**	**Cooling effect**	**Hygroscopicity**	**TypicalFood Applications**
Sorbitol	2.6	50 - 70%	Cool	Median	Sugar-free candies, chewing gums, frozen desserts and baked goods
Mannitol	1.6	50-70%	Cool	Low	Dusting powder for chewing gum, ingredient in chocolate-flavored coating agents for ice cream and confections
Xylitol	2.4	100%	Very cool	High	Chewing gum, hard candy, pharmaceuticals and oral health products.
Isomalt	2	45-65%	None	Low	Candies, toffee, lollipops, fudge, wafers, cough drops, throat lozenges
Maltitol	2.1	75%	None	Median	Hard candies, chewing gum, chocolates, baked goods and ice cream
Lactitol	2	30 - 40%	Slightly cool	Median	Chocolate, cookies, cakes, hard and soft candy and frozen dairy dessert
Erythritol	0-0.2	60 - 80%	Cool	Very low	Bulk sweetener in low calorie foods

2.1.2 Benefits of sugar alcohols

Sugar alcohols provide calories, although they provide fewer calories than regular sugars because the body absorbs sugar alcohols slowly and not completely. As a result, they enter the blood stream slower than natural sugars. Because of the incomplete absorption, sugar alcohols produce a lower blood glucose response than sugars. Therefore they have a minimal effect on blood glucose and insulin and do not cause tooth decay (oral bacteria cannot break them down). However, side effects also occur because of the incomplete absorption such as poorly digested (large amounts have a laxative effect in some people and may cause gas or bloating in others) (Kroger et al., 2006).

2.2 Isomalt

Isomalt is a unique, excellent tasting sugar-free bulk sweetener. Products made with isomalt have the same texture and appearance as those made with sugar because it is derived from sugar. Isomalt has health benefits and stability which makes it a versatile and valuable ingredient for numerous reduced-calorie foods and pharmaceuticals (Nabors and Lyn, 2002).

2.2.1 Structure of Isomalt

Isomalt is an approximately equimolar mixture of α-D-glucopyranosyl-1-6-mannitol (GPM) and α-D-glucopyranosyl-1-6-sorbitol (GPS) as shown in Figures 2.2. The industrial process yields an agglomerate of around 5% water content (Borde et al., 2002). The structural difference between GSM and GPS is confined to the carbon C-5 configuration of the acyclic polyols moiety. GPM crystallizes as a di-hydrate: the two molecules of crystallization water are fixed via hydrogen bonds to the mannitol portion, forming a double water bridge between the oxygen atoms O-2 and O-5. In this structure, the mannitol portion is in a nearly planar zigzag conformation. Crystalline GPS is reported to be anhydrous, with its sorbitol portion in a non-linear bent-chain arrangement as is D-sorbitol (Borde and Cesàro, 2001).

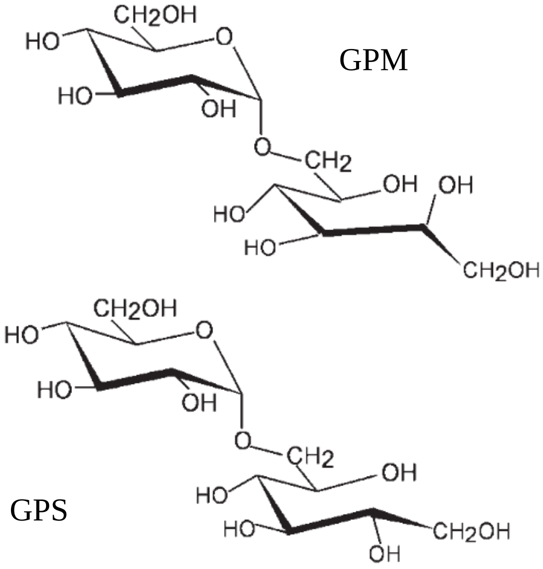


Figure 2.2 Structure of the two isomeric components of isomalt

2.2.2 Properties of Isomalt

Isomalt's nutritional and physiological benefits are ideal for use in sugar free, low calorie and diabetic products. It is particularly suitable for food and pharmaceutical applications. Table 2.2 shows physical properties of isomalt in comparison to sucrose (Grabitske and Slavin, 2008).

Table 2.2 Properties of isomalt compared to sucrose (Rose et al., 2002)

Properties	**Sucrose**	**Isomalt**
Sweetening power	100	45-65
Melting point (range)	160-185°C	145-150°C
Solution enthalpy	-18.2 kJ/kg	-39.4 kJ/kg
Cooling effect on dissolving	None	None
Solubility at 20 °C	appr.2 $\text{g/g}_{\text{water}}$	0.33 $\text{g/g}_{\text{water}}$
Hydroscopicity in powder	Low	Low
Viscosity in solution	Low	Low
Browning reactions	Median	Very low

2.2.2.1 Physiological basis

Isomalt is disaccharide polyols similar maltitol. The caloric value of isomalt have a lower energy conversion because of the stable glycoside bond, isomalt is hardly metabolized in the small intestine (Bolhuis et al., 2009). It is mainly fermented in the colon. Blood glucose response after intake of isomalt is very low so it's suitable sugar substitute for diabetics. It also possesses molecular stability which helps protect tooth decay. Isomalt cannot be broken down by enzymes from bacteria in mouth and, as result, do not release acid that can damage the tooth enamel. Extensive toxicological and metabolic studies have been conducted that prove conclusively the safe use of isomalt (Ndindayino et al., 2002).

2.2.2.2 Physical performance

Isomalt has a very low water activity at 25°C, and absorbs virtually no water up to a relative humidity of 85%.This low hygroscopicity (Table 2.2) means that isomalt can be stored easily and distributed without much special care. Further, this explains why products exclusively or mainly based on isomalt such as hard candies tend to be not sticky. In Figures 2.3 shows solubility of isomalt is much lower than that of sucrose and fructose. Because its chemical structure is not altered at normal cooking temperatures, isomalt is well suited for cooking, baking, extrusion processes, instant products and tablets (Saska et al., 2010).

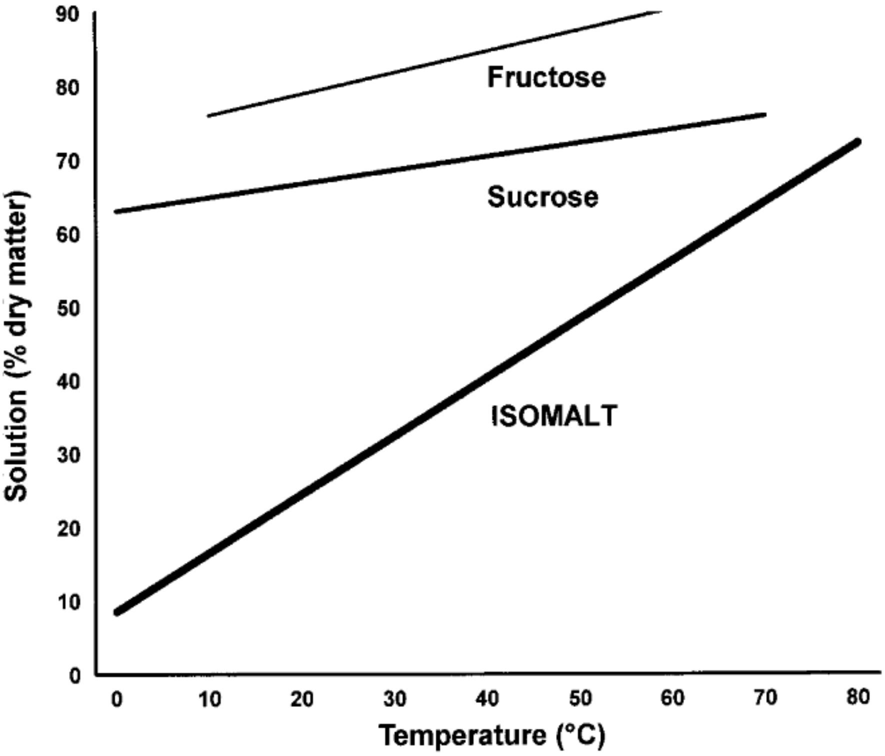


Figure 2.3 Solubility of isomalt in water compared with sucrose and fructose (Wijers et al., 2001)

2.2.2.3 Chemical stability

Isomalt provides excellent stability so it is resistant to chemical degradation. In addition, isomalt cannot undergo reaction with ingredients containing amino groups and other discoloration develops during the melting, extrusion, or baking processes. The viscosity of aqueous isomalt solutions does not differ significantly from that of corresponding sucrose solutions in a temperature range between 60 and 90°C (Sentko et al., 2006).

2.2.2.4 Sensory Properties

The sweetening potency of isomalt is between 0.45 and 0.6 compared with that of sucrose (=1.0). Isomalt has pure sweet tastes like sucrose and does not give aftertaste. Moreover, it promotes flavor transfer in food. Isomalt is often combined with reduced-calorie sweeteners such as sugar alcohol (sorbitol, xylitol, mannitol, etc.) and artificial sweeteners (aspartame, saccharin, sucralose, etc.) for to mask the bitter aftertaste of some sweeteners and bulking agents. Isomalt has a very low negative heat of solution, which is comparable to that of sucrose. Isomalt does not produce a cooling effect (Larry et al., 2009).

2.2.3 Applications of Isomalt

Isomalt is similar to sucrose and suitable sugar replacer in many areas of the various foods and pharmaceutical products. Applications of isomalt are quite versatile depending on their properties (Sentko and Willibald-Ettle, 2007), such as:

- High-boiled candies, these are very stable against water absorption because characteristics of isomalt are low solubility, high boiling point, low viscosity of the melt and high specific heat capacity.
- Low-boiled candies, pan-coated products, compressed tablets, baked goods and baking mixes because characteristics the low hygroscopicity and low solubility of isomalt.
- Chocolate jams and ice cream, no cooling effect is present when eating.
- Pharmaceutical applications because characteristics of isomalt are chemical stability, slow dissolution kinetics, low hygroscopicity and heat stability (Ndindayino et al., 2002).

Isomalt is approved as a food additive. A Generally Recognized As Safe affirmation petition was accepted for filing by the U.S. Food and Drug Administration in 1990 and it is regulated in countries worldwide, including NAFTA, EU, Japan, Australia, New Zealand, East European countries, Asian and South-American countries (Borde and Cesàro, 2001).

2.2.4 Production of Isomalt

Isomalt can be produced in the two-stage process in which sugar or sucrose is transformed by enzymatic transglucosidation into isomaltulose. Second, the isomaltulose is then hydrogenated into isomalt. The production process is illustrated in Figures 2.4.

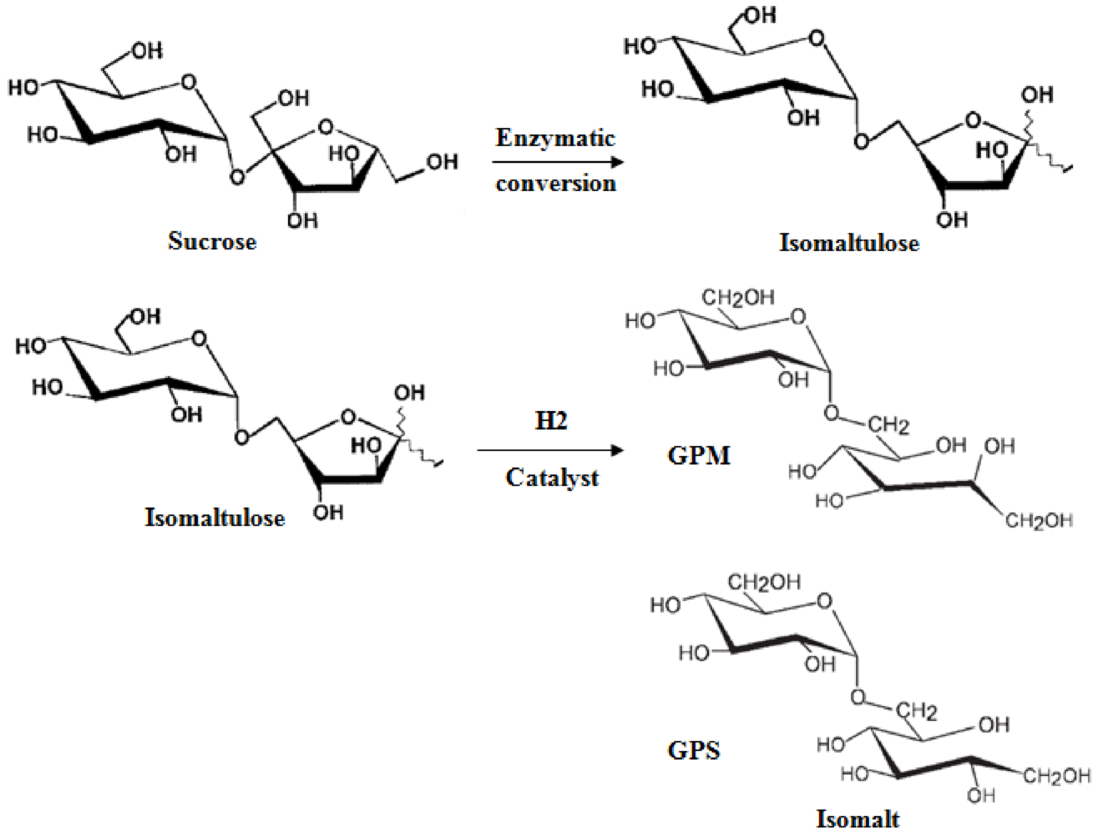


Figure 2.4 Production of isomalt from sucrose (Sentko and Willibald-Ettle, 2007)

The transformation of sugar with hydrogenation reaction needs the use of proper catalyst, often the derivation of Ni. The active Ru catalyst has also been reported to give higher activity than Ni catalyst (Eisenbeis et al., 2009). Such hydrogenation reaction needs to be performed under several control variables including temperature, pressure, type of catalyst, initial sugar concentration and other impurities that could also react with H_2.

2.2.4.1 Hydrogenation

Hydrogenation is defined as the chemical reaction between molecular hydrogen and an element or compound, usually in the presence of catalysts. Reaction possibly one in which hydrogen is added to the double bond or triple bond connecting two atoms in the structure of molecules, or one in which the addition of hydrogen results in dissociation of the molecule. Indeed, there is more hydrogenation catalyst available commercially than any other type, and for good reason, because hydrogenation is one of the most useful, versatile, and environmentally acceptable reaction routes available for organic synthesis (Khodadadi-Moghaddam et al., 2011). With the exception of a few large scales, hydrogenation products are often made on a small scale in batch reactors. Batch processes are usually most cost effective since the equipment need not to be dedicated to a single reaction (Rangel, 2005).

The catalyst is generally powdered and made slurry with reactants. The types of hydrogenation catalysts finding commercial applications include noble metals, group VIII transition metals in particular Pt, Pd, Rh, Ru, and Ni, organometallic complexes, and activated alloy catalysts that are either unsupported or support. In general, use of a support allows the active component to have a larger exposed surface area, which is particularly important in those cases where a high temperature is required to activate the active component (Koopman et al., 1981).

However, for sugar alcohol or polyols, the production of sugar alcohol with hydrogenated have many use catalysts as well as Ni catalyst (Hoffer et al., 2003), Pt catalyst (Ahmed and Kadhum, 2010), Pd catalyst (Castoldi et al., 2007) or Ru catalyst (Sifontes et al.,2010). The supports may be carbon (Heinen et al., 2000), silica (Li et al., 2002), and alumina (Eisenbeis et al., 2009) in order to obtain higher selectivity and activity. Supported catalysts may be prepared by a variety of methods, depending on the nature of active components as well as characteristics of carrier for examples, decomposition, impregnation, precipitation, coprecipitation, adsorption, or ion exchange. Both low and high surface area materials are employed as carriers (Nishimura, 2001). Although the selection of the metal is of course essential, the choice of the support, the way of catalyst preparation and the way of catalyst activation are also important factors in designing a catalyst. Furthermore, the hydrogenation reaction needs to be performed under several control variables including temperature, pressure, type of catalyst, initial sugar concentration and other impurities that could also react with H_2. Lack of literature in this area makes it difficult to assemble and optimize the production system for isomalt. Accordingly, the studies of isomalt production from isomaltulose hydrogenated with catalyst. Literature review concerning this method is elucidated in Table 2.3.

Table 2.3 Literature review on hydrogenation of sugar alcohol

Author	Raw material	Product	Catalyst	Catalyst characterization	Condition/Variable	Conclusion
Zhang et al., 2011	Glucose	Sorbitol	5%Ru/MCM-41	Pulse chemisorptions, XRD, SEM	Reactor: Parr 5500 batch reactor Initial sugar concentration: 10% (g/mL) glucose H_2 pressure: 30 bar Temperature: 100-140˚C Reaction time: 1-6 h Stirrer speed: 500 rpm	- Optimum condition: Temperature= 120˚C Reaction time= 2 h H_2 pressure= 30 bar - Highest yield achieved: 94.43% of sorbitol
Geyer et al., 2011	Glucose	Sorbitol	Ni on ZrO_2, TiO_2, ZrO_2/TiO_2, SiO_2, $MgO/SiO_2/Al_2O_3$ particle fraction <63 mm	XRF, XRD, CO chemisorption	Calcination: Flow rate 120 l/h air 450°C 6h Ruduction: flow of H_2 0.5 Mpa, 400°C 5°C/h 4 h Stabilization condition: N_2 60 l/h 50-60°C 12 h Initial sugar concentration: 50%(w/w) H_2 pressure: 120 bar Temperature: 120 ˚C Reaction time: 1-4 h Catalyst loading: 1.47 - 5.56 g Stirrer speed: 1800-2500 min^{-1}	- Optimum condition: Temperature= 120˚C Reaction time= 1 h H_2 pressure= 120 bar Catalyst loading= 1.5 g Stirrer speed= 2500 min^{-1} - Highest yield achieved: Ni/SiO_2 got an enhanced hydrogen activity, better selectivity and higher stability of metal dispersion. Crystallite size: Ni/ZrO_2 7.6 nm, Ni/SiO_2 9.6 nm

Table 2.3 Literature review on hydrogenation of sugar alcohol (continued)

Author	Raw material	Product	Catalyst	Catalyst characterization	Condition/Variable	Conclusion
Sifontes et al., 2010	-D-maltose -D-galactose -L-rhamnose -L-arabinose	- D-sorbitol - D-galactitol - L-rhamnitol - L-arabitol	2.5% Ru/activated Carbon	TEM, SEM , ICP-OES, Nitrogen adsorption	Reactor: Parr 4561 batch reactor (300 ml) Initial sugar concentration: 10%(w/w) H_2 pressure: 30-180 bar Temperature: 80-150 °C Reaction time: 3 h Stirrer speed: 1800 rpm	-Optimum condition: Temperature= 130°C H_2 pressure= 60 bar -Highest yield achieved: - 100% of L-arabitol - 100% of L-rhamnitol - 98% of D-galactitol - 76% of D-sorbitol
Eisenbeis et al., 2009	Glucose	Sorbitol	8% ruthenium on γ-Al_2O_3	BET, SEM, XRD, TPR	Calcination: in air, heating rate 2K/min at 350°C, 4h Initial sugar concentration: 40 wt% glucose H_2 pressure: 80 bar Temperature: 100-140 °C Stirrer speed: 500 min^{-1}	-Optimum condition: Temperature= 140°C H_2 pressure= 80 bar
Castoldi et al., 2009	- Glucose - Fructose	-Sorbitol -Mannitol	-5% Ru/C -Nickel-Raney catalysts	-	Reactor: Parr 4531 batch reactor (1 L) H_2 pressure: 750 psia (51.71 bar) Temperature: 130 °C Reaction time: 0-4 h	-Optimum condition: Temperature= 130°C Reaction time= 3 h H_2 pressure= 750 psia -Highest conversion achieved: 100% of glucose conversion on 5%Ru/C

Table 2.3 Literature review on hydrogenation of sugar alcohol (continued)

Author	Raw material	Product	Catalyst	Catalyst characterization	Condition/Variable	Conclusion
Kuusisto et al., 2008	Lactose	Lactitol	- 5% Ru/C (Johnson Matthey) - 5% Ru/Al_2O_3(Fluka) - 5%Ru/silica(synthesized) - 5% Ru/TiO_2 (synthesized) - 5%Ru/MgO (synthesized)	BET, SEM-EDXA, XRF, hydrogen TPD	Reactor: Parr 4843 batch reactor (300 mL) Initial sugar concentration: 40 wt% d-lactose H_2 pressure: 40-60 bar Temperature: 110-130 °C Stirrer speed: 1800 rpm	- Optimum condition: Temperature= 120°C Reaction time= 3 h H_2 pressure= 50 bar - Highest yield achieved: 100% of Lactitol on 5% Ru/C
Liu et al., 2008	Glucose	Sorbitol	- 6.1%RuC(HY) - 6.3%RuC(SBA15) - 6.1%Ru/C-HY-H - 5.9%Ru/C-SBA15-H - 5.4%Ru/HY-H - 5.7%Ru/SBA15-H - 5%Ru/C - Ni65	TEM, BET	Reactor: Parr batch reactor (300 mL) Initial sugar concentration: 40% (g/mL) glucose H_2 pressure: 80 bar Temperature: 100°C Reaction time: 3 h Catalyst loading: 0.05 g Stirrer speed: 300 rpm	- Optimum condition: Temperature= 100°C Reaction time= 3 h H_2 pressure= 80 bar - Highest conversion achieved: 56% of glucose conversion on 6.3%RuC(SBA15)
Castoldi et al., 2007	Glucose	Sorbitol	- 10%Pt/C(synthesized) - 5%Ru/C(Degussa Brasil Ltda)	-	Reactor: Parr 4842 batch reactor (100 mL) Initial sugar concentration: 40 wt% glucose H_2 pressure: 80 bar Temperature: 100-110°C Reaction time: 30 min	- Optimum condition: Initial sugar Temperature= 100°C Reaction time= 30 min H_2 pressure= 80 bar - Highest conversion achieved: 99% conversion on 5%RuC

Table 2.3 Literature review on hydrogenation of sugar alcohol (continued)

Author	Raw material	Product	Catalyst	Catalyst characterization	Condition/Variable	Conclusion
Pan et al., 2007	Glucose	Sorbitol	- 5%Ru/MWNT(multi-wall carbon nanotubes) - 5%Ru/Al_2O_3 - 5%Ru/SiO_2 - Raney Ni	XRD, XPF, TEM	Initial sugar concentration: 48% (g/mL) aqueous glucose H_2 pressure: 40 bar Temperature: 80-120°C Reaction time: 1-4 h Catalyst loading: 0.05 g Stirrer speed: 1200 rpm	- Optimum condition: Temperature= 120°C Reaction time= 2 h H_2 pressure= 40 bar -Highest conversion achieved: 62.5% of glucose conversion on 5%Ru/MWNT
Hoffer et al., 2003	Glucose	Sorbitol	- 4.9%Ru/C(Engelhard) - 3.5%Ru/C(Engelhard) - 5.1%Ru/C(Dep.-prec.) - 5.6%Ru/C(Anionic-dep.) - RaNi(Engelhard) - RaNi-Mo(Engelhard) - RaNi-Cr/Fe(Engelhard)	ICP-OES, H2-chemisorption	Reactor: Gas-induced stirrer(Premex AG) Initial sugar concentration: 10% (g/mL) glucose H_2 pressure: 4.0–7.5MPa Temperature: 120°C Reaction time: 0-140 min	- Optimum condition: Temperature= 120°C Reaction time= 140 min H_2 pressure= 4.0 MPa - Highest selectivity achieved: >98% of sorbitol on all catalyst

CHAPTER III

EXPERIMENTAL

This chapter describes the experimental systems and procedures used in this study. It is divided into three parts consisting of catalyst preparation, catalyst characterization and hydrogenation experiments. The first part explains catalyst preparation by the impregnation method. The second part illustrates the details of catalyst characterization techniques containing N_2 physisorption (BET), X-ray diffraction (XRD) and X-ray fluorescence (XRF). Finally, a detailed production procedure for isomalt with hydrogenation of isomaltulose is described.

3.1 Catalyst Preparation

3.1.1 Material

The chemicals used in the catalyst preparation are all analytical grades as listed in Table 3.1.

Table 3.1 Details of chemicals used in catalyst preparation

Chemicals	Formula	Manufacture
1. Ruthenium (III) nitrosyl nitrate solution	$Ru(NO)(NO_3)_x(OH)_y$, x+y=3	Sigma-Aldrich Cheme GmbH, Germany
2. Charcoal activated powder	C	Panreac, Belgium

3.1.2 Impregnation method

The Ru-promoted/C samples are prepared by incipient impregnating activated carbon (Aldrich) using water as solvent, ruthenium (III) nitrosyl nitrate solution (Aldrich) as a metal precursor loading 5 wt%(5Ru/C) and 10 wt%(10Ru/C) Ru on the supports. The amount of solution used is slightly greater than the pore volume of the activated carbon support. After impregnation, the catalysts are dried in air overnight at 120 ºC and then calcined in Ar at 500ºC with the flow rate 30 cm^3/min for 4 h. Before use, catalysts samples are reduced at 200 ºC for 2 h under flowing H_2 (Xiaobo et al., 2007).

3.2 Catalyst characterization

3.2.1 X-ray fluorescence Spectrometer (XRF)

X-ray fluorescence is the emission of X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals. The catalyst sample will be observed using PHILIPS PW 2400. This instrument has located at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

3.2.2 N_2 physisorption (BET)

The BET surface area for the multipoint is measured by N_2 physisorption using BEL SORP mini II. The catalysts are firstly pretreated in helium gas flow of 50 ml/min at 150ºC for 3 h. Sample pretreatment system are used to remove water bound to the particle surface from air moisture. After cooled down to the ambient temperature, the weight of dried catalyst is collected. Sample cell is installed to the adsorption part. The requisite data is input to the software before the measurement. The sample cell is dipped in the dewar containing liquid N_2. The volume of N_2 is measured at -196 ºC using the different N_2 partial pressure. This instrument has located at Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University.

3.2.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of powder are obtained using an X-ray diffractometer SIEMENS D500 connected with a computer with Diffract ZT version 3.3 programs for fully control of the XRD analyzer. The experiments are carried out using Ni-filtered CuKa radiation. Scans are performed over the 2θ ranges from 10º - 80º. The crystalline size is estimated from line broadening according to the Scherrer equation and a-alumina is used as standard. This instrument has located at Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University.

3.2.4 Hydrogen Temperature Programmed Reduction (H_2-TPR)

H_2 consumption for reduction of metal oxides to metal state was determined using 5.04 % H_2 in Nitrogen as reducing gas. Approximately 0.1 g of catalyst was introduced to Thermo Finnigan (TPDRO 1100) equipped with TCD detector. Prior to the reduction step, catalyst was heated up from room temperature to 800^{o}C at a ramp rate of 10^{o}C min^{-1} in flowing nitrogen gas with a flow rate of 20 cc min^{-1} and was held for 4 hours. After that, the catalyst was cooled down to room temperature and then 5.04% H_2 in Nitrogen with a flow rate of 20 cc min^{-1} was introduced to the system and ramping from room temperature to 800^{o}C at 10^{o}C min^{-1}.

3.3 Hydrogenation experiments

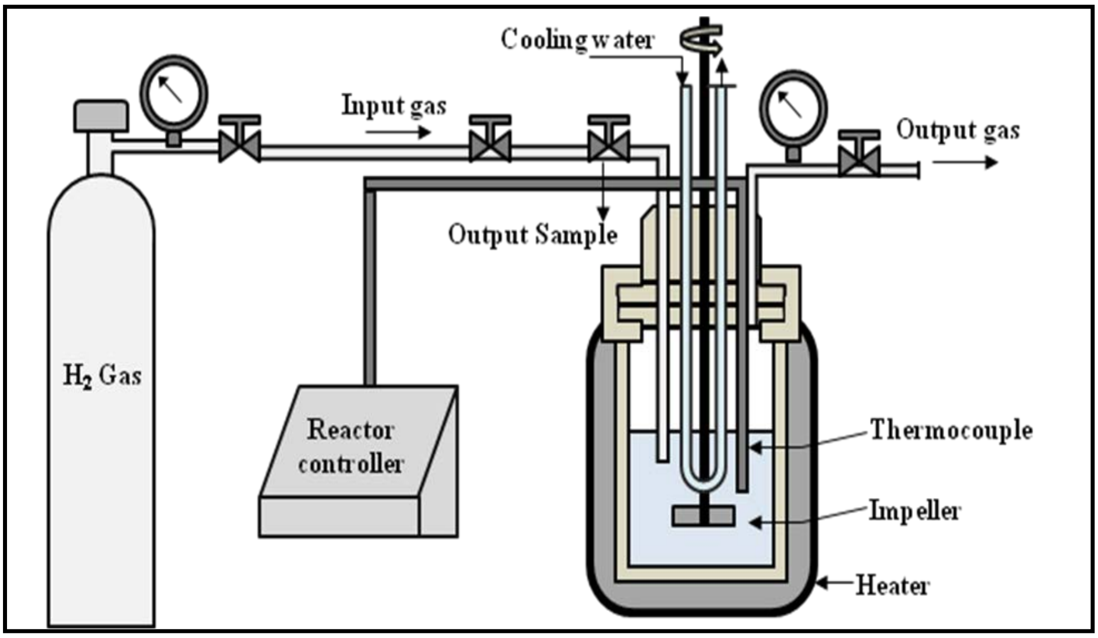


Figure 3.1 Diagram of reaction equipment for hydrogenation of isomaltulose

The reactions are carried out in a stainless steel reactor, model 4531, with a volume of 300 ml. Isomaltulose (40 wt% in water) is prepared with distilled water (80-130 ml). The solution is introduced into the reactor while the pressure is regulated. The reaction is carried out at 100-130ºC and a pressure of 30-50 bar. The impeller rate is fixed at 670 rpm. The temperature, total pressure is recorded during the reaction. The samples are taken from the reactor with the reaction time of 1 to 8 h and analyzed by HPLC.

3.3.1 Kinetic of isomaltulose hydrogenation

A series of experiments are carried out with the purpose of studying the kinetic characteristic of the hydrogenation reactions of isomaltulose. A set of experiments is performed under varying conditions of pressure (30, 40 and 50 bar), time (1, 2, 3, 4, 5, 6, 7 and 8 h), initial sugar concentration (40%) and temperature (100ºC, 120ºC and 130ºC) in the presence of a supported Ru/active carbon catalyst with a loading of 5%(w/w) and 10%(w/w). The impeller rate is fixed at 670 rpm.

3.3.2 HPLC analysis of isomalt

The products of the reaction are analyzed by high-performance liquid chromatography (HPLC) with APS-2 Hypersil column (Length 250 mm , I.D. 4.6 mm, Particle size 5 µm), with the following conditions: 30 ºC, flow rate of 1 mL/min (Detector : Refractive Index , Waters) using a mobile phase of acetonitrile/DI water (75:25, v/v).

CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into four major sections. In the first section, the characterization of the ruthenium supported on charcoal activated powder was investigated. Next, the effects of operating conditions on the hydrogenation of isomaltulose were evaluated. The third section shows the stability of 10%Ru/C catalyst for hydrogenation of isomaltulose. The forth section is the determination of kinetic parameters of the hydrogenation reaction.

4.1 Characterization of the Ru/C catalyst

In this section, the Ru/C catalysts prepared from impregnating Ruthenium (III) nitrosyl solution (as Ru precursor) on charcoal activated powder catalysts were characterized for their surface area, pore volume, and pore size by nitrogen physisorption.

Two gases, i.e. air (dry air), and argon (inert gas), were examined for their effectiveness in the calcination of the catalysts (Yin et al., 2004). Figure 4.1(a) shows that 5%Ru/C catalysts after calcined with dry air exhibited a non-glossy, grey powder and Figure 4.1(b) shows that 5%Ru/C and 10%Ru/C catalysts after calcined with argon were non-glossy, black powders.

Table 4.1 demonstrates that there was a weight loss when using dry air which indicated the decomposition of the charcoal powder support (Mudd et al., 2001). This might deteriorate the stability of the resulting catalyst. Therefore argon was selected as the preferred calcined gas to avoid such decomposition.

Table 4.1 Weight loss from calcination

Catalyst	Initial weight (g)	Final weight (g)	Weight loss (g)	Weight loss (%)
Ru/C calcined with Ar	2	1.9846	0.0154	0.77
Ru/C calcined with dry air	2	0.5291	1.4709	73.55

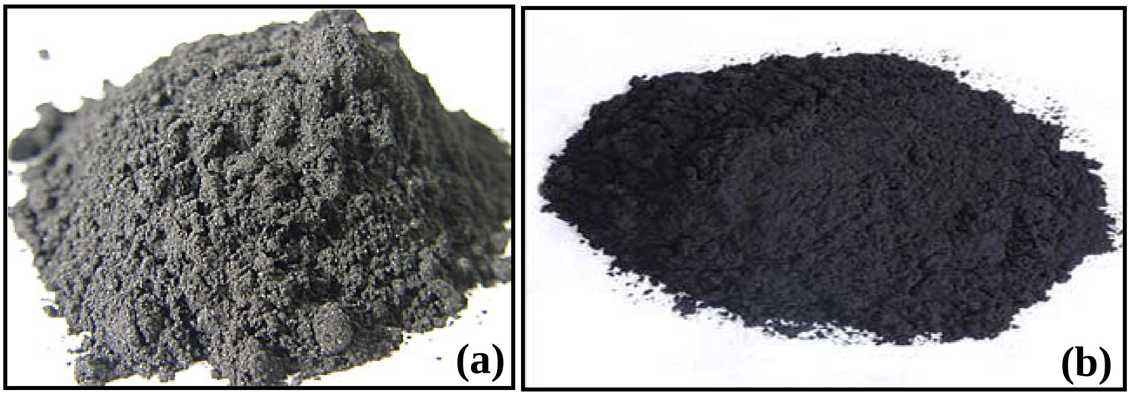


Figure 4.1 Ru/C catalysts: (a) 5%Ru/C catalysts calcined with dry air, (b) 5%Ru/C and 10%Ru/C catalysts calcined with argon

4.1.1 N_2 physisorption

The charcoal activated powder supports and Ru/C catalyst were tested for their surface area, pore volume and pore size using adsorption and desorption measurement with nitrogen gas at 77 K. The results from this measurement are shown in Table 4.2.

The pore size distribution curve of carbon supports and Ru/C catalysts were derived from the Barrett-Joyner-Halenda (BJH) method using the adsorption branch. Figures 4.2-4.3 show the N_2 adsorption/desorption isotherms and the pore size distribution of charcoal carbon supports and Ru/C catalysts. All samples display Type I adsorption curve with hysteresis loops in the P/P_0 range of 0–1. Isotherms are given by mesoporous solids having relatively small external surface and mesoporous adsorbents for subcritical and supercritical conditions (Sangwichien et al., 2002). This indicates the existence of mesoporous structure within the catalyst (Corma, 1997) consistent with results of the mean pore diameter in Table 4.2 and Figures 4.2-4.3(inset).

Table 4.2 shows that the BET surface area of fresh activated carbon supports was 660 m^2 g^{-1}. The addition of Ru 5wt% on carbon support after calcined with dry air and argon gave the surface area of 624 and 636 m^2 g^{-1}, respectively which were only slightly lower than the surface area of fresh activated carbon supports, maybe because ruthenium loaded into the pore of the support caused a slight pore blockage. Particularly with dry air, the dry air destroyed the structure of carbon supports (as shown by XRD patterns in Figure 4.4 and will be discussed later), and this was confirmed with the weight loss data in Table 4.1. Therefore although the surface area did not seem to be significantly different, the yield of the catalyst was extremely low with dry air. In other words, with 73.55% weight reduction (Mudd et al., 2001), the calcination with dry air seemed to be unrealistically technically feasible.

The addition of Ru 10 wt% on supports before and after the calcination with argon provided the surface area 604 and 665 $m^2\ g^{-1}$, respectively, and the weights of catalyst before and after calcination with argon were 2 and 1.97 g, respectively. This demonstrates that the weight loss was not significant and that the impurity before calcination might have caused some blockage of the pores which led to an apparently slightly lower surface area. This impurity was removed after calcination and a higher surface area was observed.

The pore volumes of 5% Ru/C after calcined with dry air and argon were 143.3 and 146.0 $cm^3\ g^{-1}$ (error ± 5%), respectively, while pore diameters were found to be similar. The 10% Ru/C catalyst after calcined with argon had the pore volume of 152.8 $cm^3\ g^{-1}$ and the pore diameter was 2.8 nm.

Table 4.2 Surface area, pore volume, and pore size of the support and Ru/C catalyst by N_2 physisorption

Catalysts	Pretreatment condition	Surface area[a] ($m^2\ g^{-1}$)	Pore volume[a] ($cm^3\ g^{-1}$)	Pore diameter[a] (nm)	Initial weight (g)	Final weight (g)
Support	None	660	151.8	2.9	2	2
5%Ru/C	773 K, Dry air	624	143.3	3	2	0.53
5%Ru/C	773 K, Ar	636	146	3	2	1.98
10%Ru/C	773 K, Ar	665	152.8	2.8	2	1.97

[a] Using N_2 physisorption at -196 °C: Error of measurement ± 5%

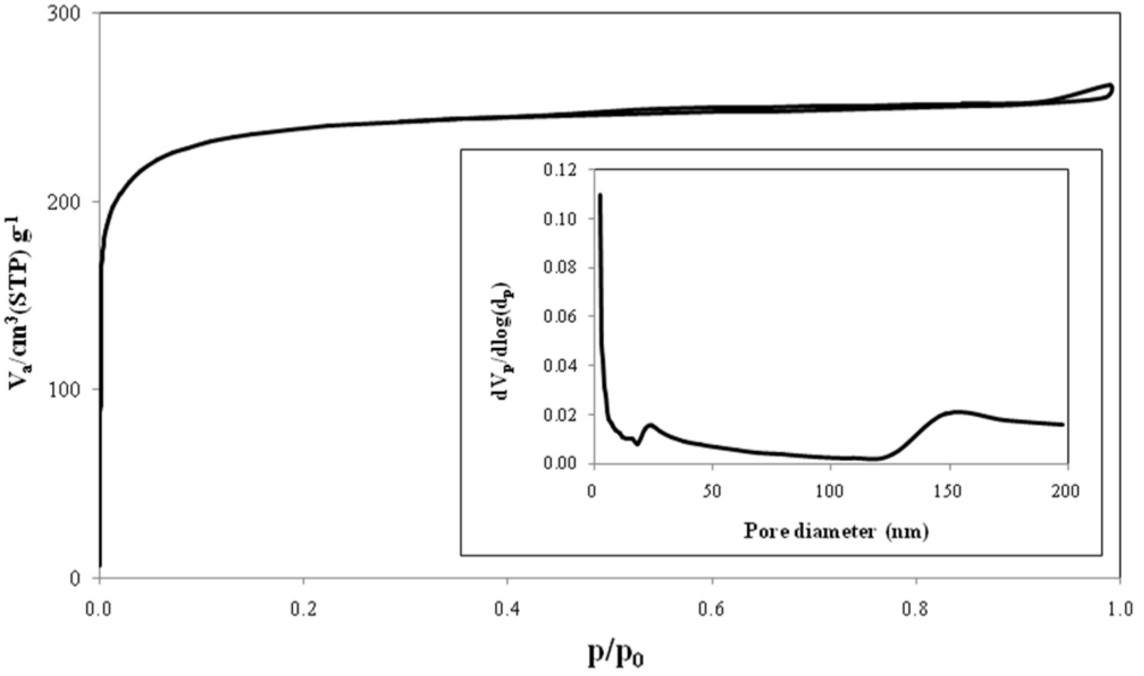


Figure 4.2 N_2 adsorption/desorption isotherms and the pore size distribution (inset) of the fresh support (charcoal activated powder)

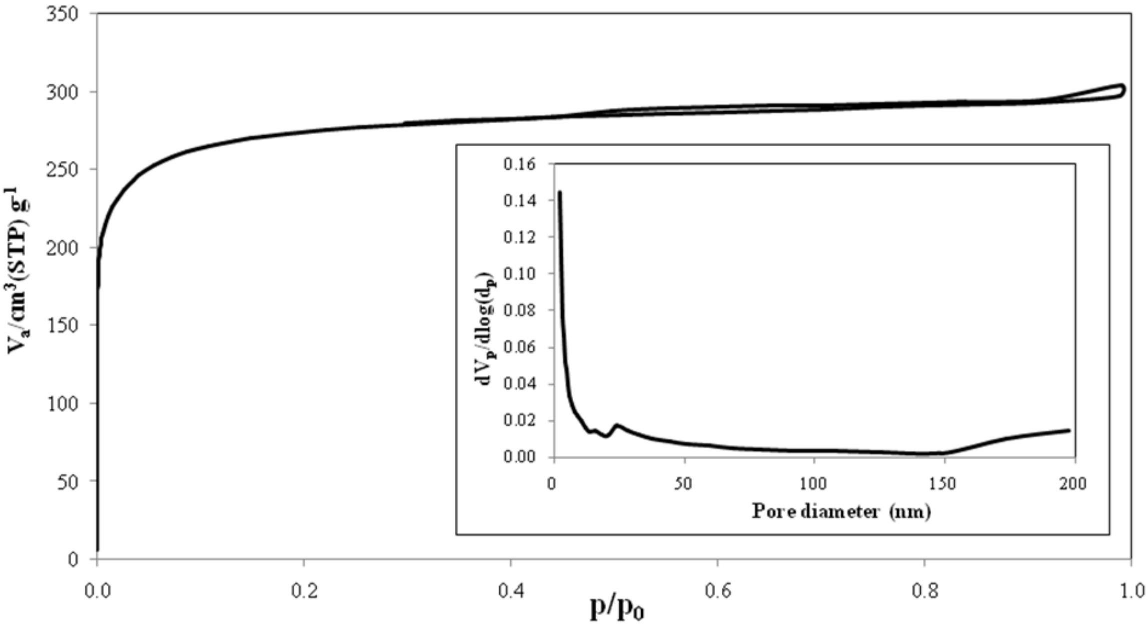


Figure 4.3 N_2 adsorption/desorption isotherms and the pore size distribution (inset) of the 10%Ru/C after treatment with argon

4.1.2 X-ray diffraction (XRD)

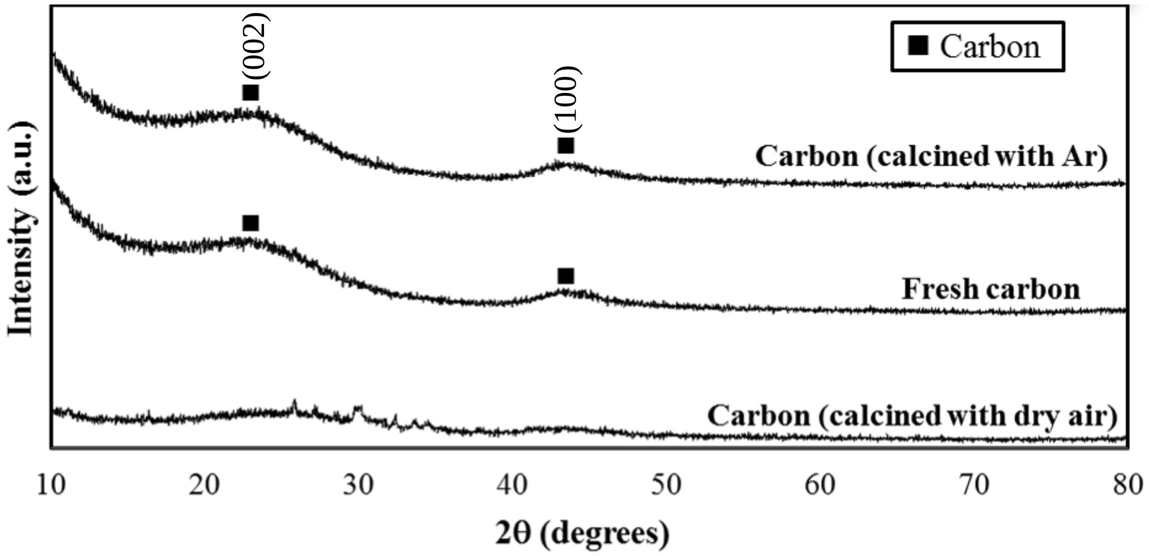


Figure 4.4 XRD patterns of the carbon supports

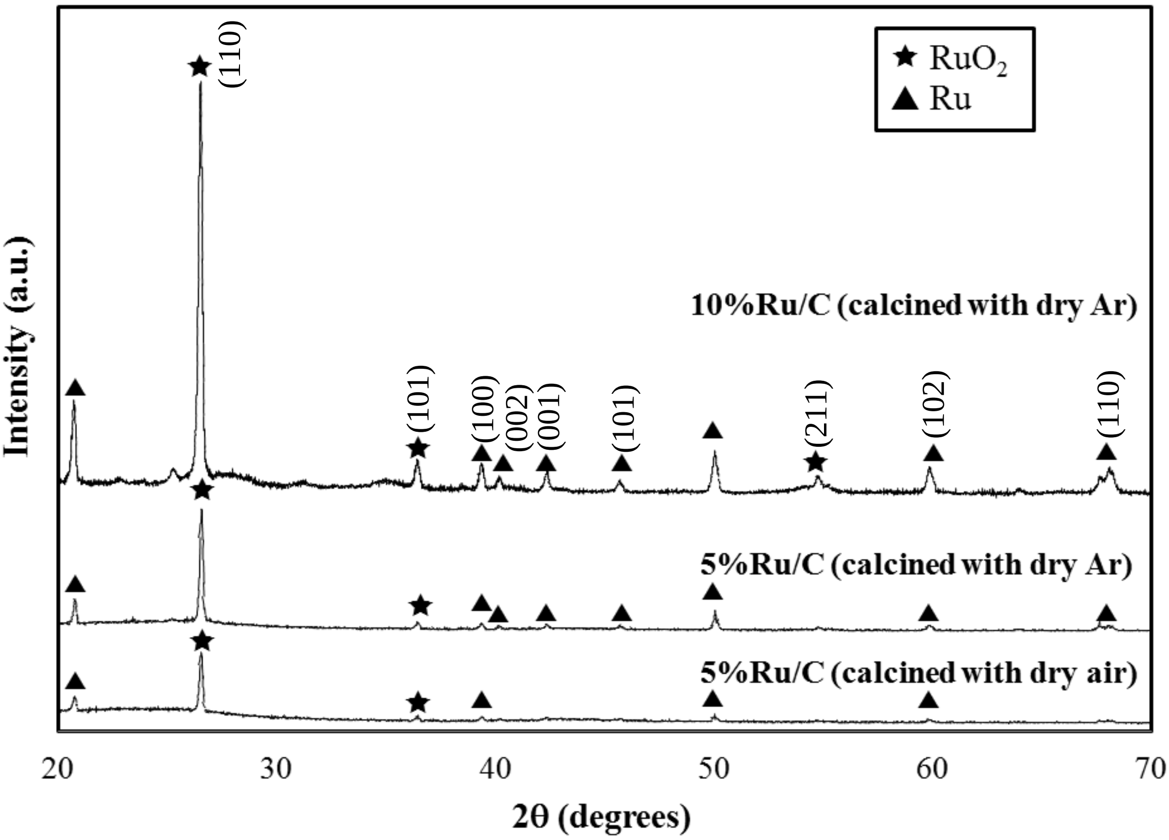


Figure 4.5 XRD pattern of the composite ruthenium catalysts

Figure 4.4 shown patterns of the fresh carbon supports and carbon supports after calcined with dry air and argon at 500 °C. The XRD patterns recorded before and after calcined with argon characteristic peaks corresponding to carbon, the diffraction peaks at 2θ values of 26.5° and 42.4° observed in the diffraction of carbon could be attributed to the hexagonal graphite structures (002), and (100) plane (shown as■). Graphite structures were not observed in the supports when calcined with dry air, which may be because carbon was decomposed with dry air at high temperature. Ru incorporated with carbon by impregnation (5%Ru/C (Ar)) after calcined with argon had XRD patterns as displayed in Figure 4.5 which contained the peaks at around 26.51° and 36.4°. These were indexed to (110) and (101) (shown as★) diffraction planes of anhydrous crystalline RuO_2 (JCPDS Card No. 43-1027) with a rutile-type structure (Tomohisa et al., 2007), whereas the peaks at 39.4°, 41.8°, 42.3°,45.7°, 59.8° and 68.0° seen on catalysts could be respectively assigned to (100), (002), (001), (101), (102) and (110) (shown as▲) diffraction planes of bulk hexagonal Ru metal (JCPDS card No. 06-0663) (Fabing et al., 2007). Due to the higher amount of Ru, the XRD pattern of 10%Ru/C was clearer with more peaks than that of 5%Ru/C catalysts. Calcination with air, on the other hand, only displayed weak peaks which may be due to a very small crystallite size.

After Ru loading and calcined with dry air and argon, both Ru and RuO_2 were found to exist in all catalyst samples, and according to Petr et. al. (1995), this should be effective for the hydrogenation of isomaltulose.

Table 4.3 Crystallite size from XRD line broadening for charcoal activated powder (supports), and Ruthenium based catalysts

Catalysts	Ru crystallite size (nm)	RuO_2 crystallite size (nm)
5%Ru/C (Dry air)[a]	2.12	4.53
5%Ru/C (Ar)[b]	2.18	5.25
10%Ru/C (Ar)[c]	3.74	5.65

[a] 5%Ru/C catalysts calcined with air zero

[b] 5%Ru/C catalysts calcined with argon

[c] 5%Ru/C catalysts calcined with argon

The crystallite size of carbon supports RuO_2 and Ru metals obtained by XRD line broadening are shown in Table 4.3 and this indicates that the mean crystallite size of fresh support, carbon after calcined with air zero and argon, 5%Ru/C after calcined with air zero, 5%Ru/C after calcined with argon and 10%Ru/C after calcined with argon for Ru metal between 2 and 4 nm, and for RuO_2 4 and 6 nm.

4.1.3 X-ray fluorescence Spectrometer (XRF)

The prepared Ru/C was characterized by XRF to determine Ru content on the surface catalysts. Table 4.4 illustrates the amount of Ru and the loading percentage which was close to the amount of Ru during the impregnation. This indicates that Ru could be successfully loaded on to the activated carbon surface. Note that in case of calcinations in air, loss of carbon support during calcinations resulted in higher Ru content.

Table 4.4 Ru content of catalyst after calcined with different gas

Catalysts	Ru loading[a] (wt.%)
5%Ru/C(Dry air)	35.0
5%Ru/C(Ar)	5.1
10%Ru/C(Ar)	12.2

[a] measured with X-ray fluorescence spectrometer

4.1.4 Hydrogen Temperature Programmed Reduction (H_2-TPR)

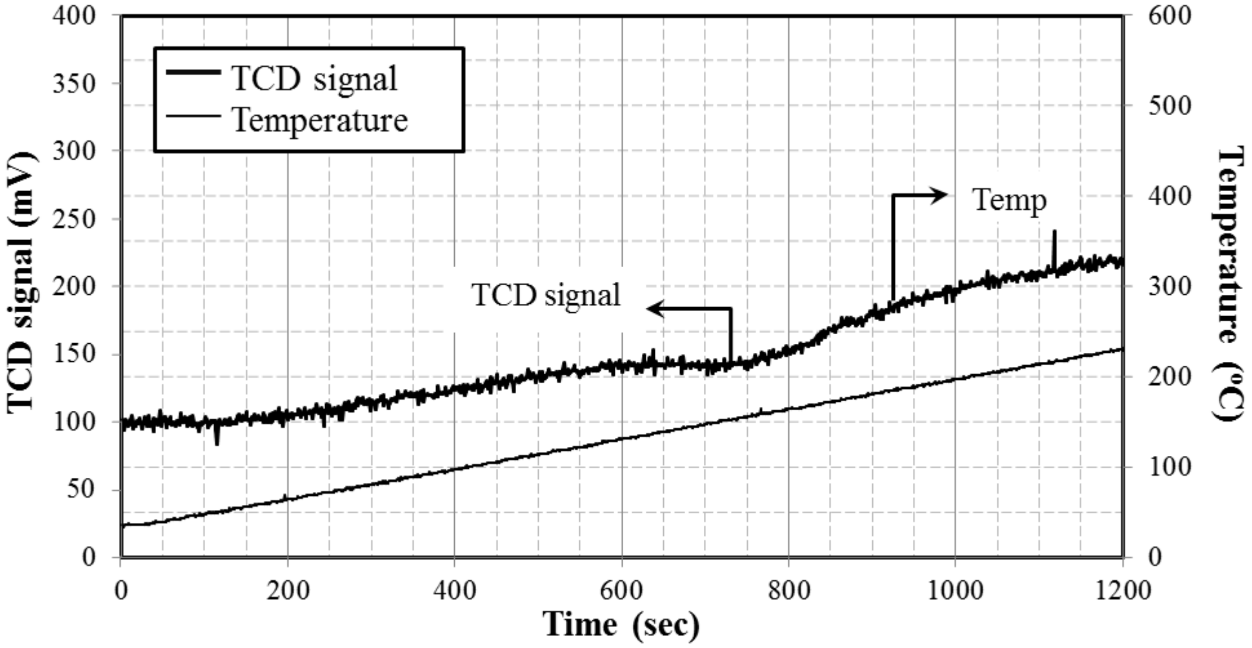


Figure 4.6 H_2-TPR of 5%Ru/C calcined with Ar

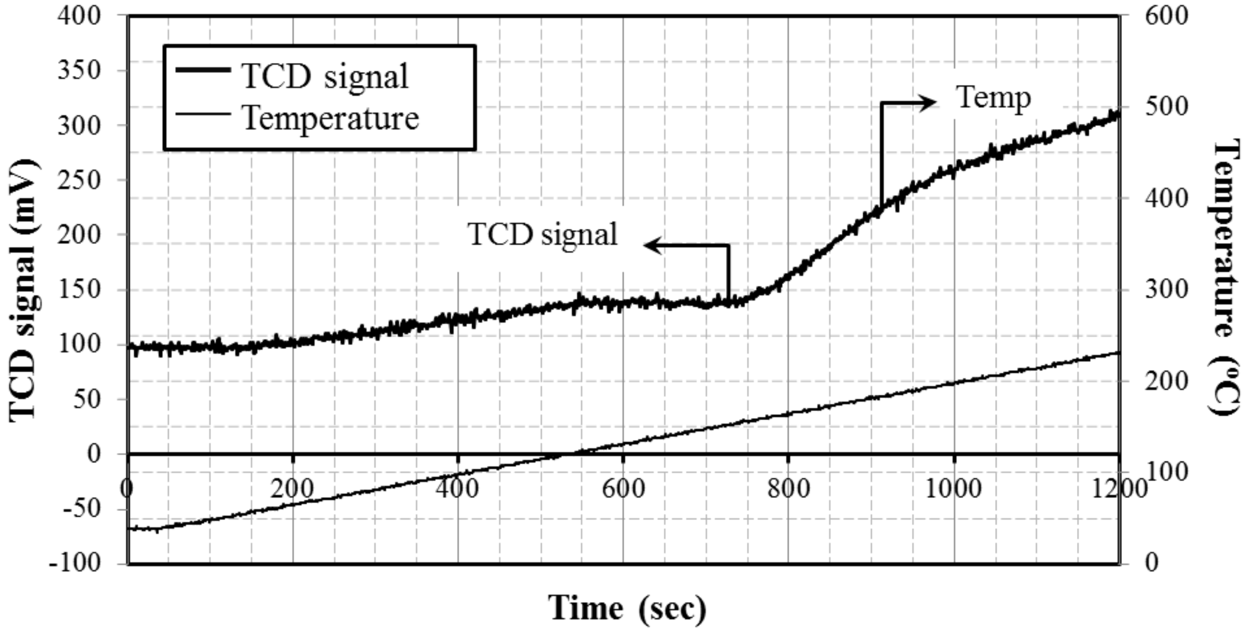


Figure 4.7 H_2-TPR of 10%Ru/C calcined with Ar

The Ru/C catalyst in forms of metal oxides such as RuO_2 was characterized by reducing from the oxide form to metal form such as Ru. This technique was used to determine the reducibility of the catalysts for evaluating ability to reform the form of metal oxide to metal. Figures 4.6 and 4.7 show the reduction profiles of the 5%Ru/C and 10% Ru/C catalysts where the reduction temperature of the catalysts was observed at 150^{o}C. Therefore the reduction of Ru samples at 200°C for 2 h as employed in this work was adequate for the complete reduction reduction of ruthenium and the Ru/C catalysts were effective for hydrogenation of isomaltulose.

4.2 Effects of operating condition on hydrogenation of isomaltulose

This section describes the work on the determination of activity and performance of the Ru/C catalyst for the hydrogenation of isomaltulose (40 wt% initial isomaltulose concentration) in the pressure vessel stirring reactor. To minimize the external mass transfer resistance, the impeller speed was maintained at a maximum speed of 670 rpm. The standard condition of the hydrogenation of isomaltulose is provided in Table 4.5.

Table 4.5 Standard operating condition for hydrogenation of isomaltulose

Catalyst	Temperature (°C)	Pressure (bar)	Catalyst :isomaltulose (g ml^{-1})	Volume of isomaltulose (ml)	Head space of reactor (ml)	Concentration of isomaltulose (%wt)
Ru/C	120	50	3.58×10^{-3}	139	78	40

4.2.1 Effect of gas in calcination catalyst

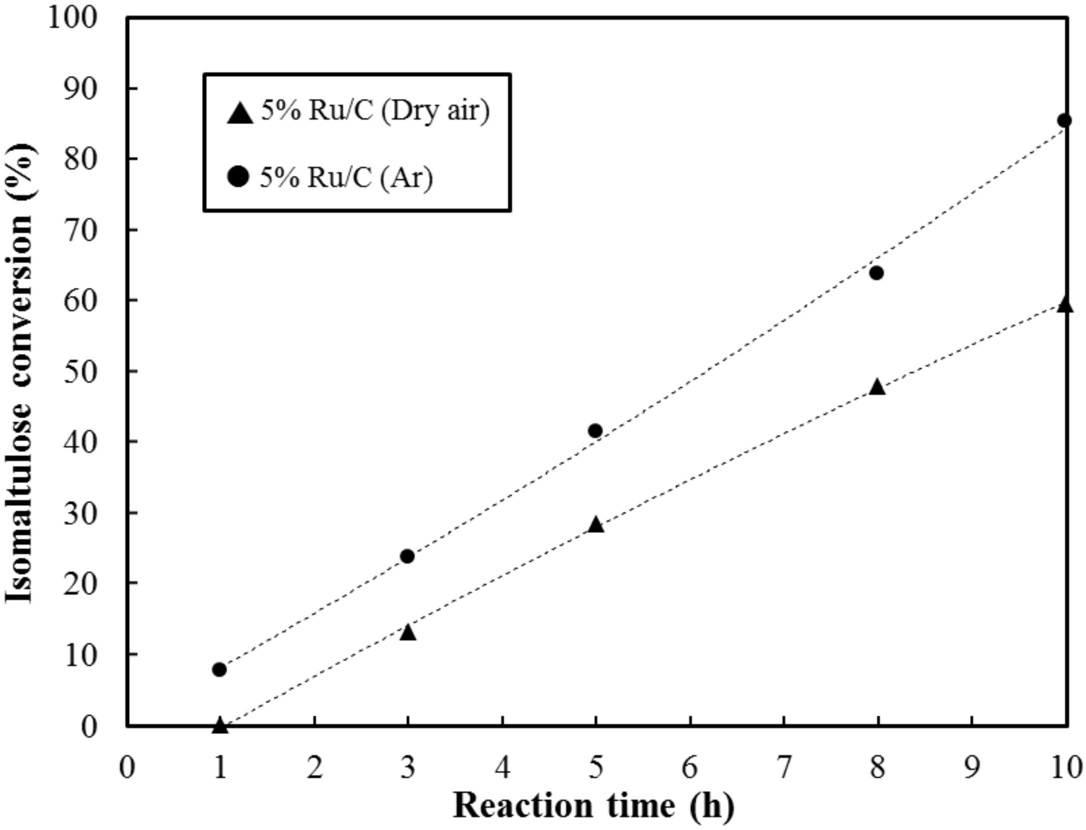


Figure 4.8 Effect of gas type in calcinations of 5%Ru/C catalyst on isomaltulose conversion (standard operating condition)

The test in this section is for the hydrogenation of isomaltulose with 5% Ru/C catalysts where the effect of gas type, i.e. air without moisture (dry air) and Ar employed in the calcination step on the reaction performance, is shown in Figure 4.6. It can be seen that the 5%Ru/C calcined in Ar exhibited higher isomaltulose conversion than that calcined in air at the reaction period of 10 h. Isomaltulose conversion of 85.3% and 59.5% could be obtained within 10 h with 5%Ru/C (Ar) and 5%Ru/C (dry air) catalysts, respectively. The lower catalytic activity of 5%Ru/C (dry air) catalyst might be due to the loss of surface area during the calcination step (Table 4.2) and perhaps the loss from the oxidation of Ru metal. It should be mentioned that the selectivity of isomalt product was quite close to 100% for the whole reaction period, for both catalysts. Therefore isomaltulose conversion could represent directly the isomalt yield.

4.2.2 Effect of catalyst metal loading

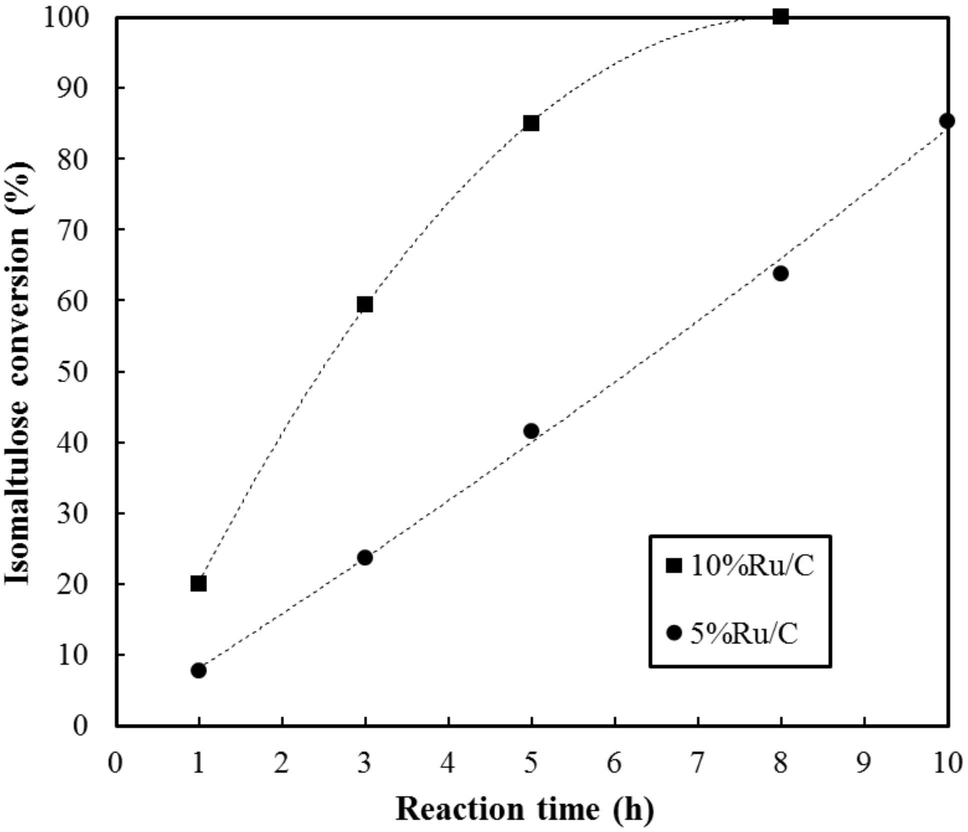


Figure 4.9 Effect of ruthenium loading on isomaltulose conversion

Table 4.6 Effect of ruthenium loading at temperature120°C, pressure 50 bar

Condition	**%loading of Ru**	
	5%	**10%**
Volume of isomaltulose solution (ml)	139	139
Head space of reactor (ml)	78	78
Ratio of weight catalyst[a] (g ml^{-1})	3.60×10^{-3}	3.60×10^{-3}
Ratio of weight Ru[b] (g ml^{-1})	1.80×10^{-4}	3.60×10^{-4}
TOF[c] ($mol_{isomaltulose}\ s^{-1}\ mol_{Ru}^{-1}$)	1.36×10^{-2}	1.32×10^{-2}
Initial rate of reaction[d] (mol l^{-1} s^{-1})	2.59×10^{-5}	7.89×10^{-5}
k^e ($s^{-1}\ g_{metal}^{-1}$)	1.50×10^{-3}	1.57×10^{-3}
Isomalt completion time(h)	10	8

[a] Ratio of weight catalyst (g ml^{-1}) =Amount of catalyst (g)/Volume of isomaltulose solution (ml)

[b] Ratio of weight Ru (g ml^{-1}) = Amount of Ru (g)/ Volume of isomaltulose solution (ml)

[c] TOF ($mol_{isomaltulose}\ s^{-1}\ mol_{Ru}^{-1}$) = Isomaltulose converted (mol)/total mole of Ru metal (mol)×time (s)

[d] Initial rate of reaction from Equation 4.2

[e] Kinetic constant (*k*) from Equation 4.3

The effect of Ru loading on isomaltulose conversion is shown in Figure 4.7. Isomaltulose conversion increased with increasing Ru content from 5 to 10%. Isomaltulose could be completely converted to isomalt within 8 h at Ru loading of 10%. It is therefore clear that the conversion could be enhanced simply by increasing the amount of metal active species. Table 4.6 indicates that the reaction rate constants (*k*) for isomaltulose hydrogenation over 5%Ru/C and 10%Ru/C were quite similar at 1.50×10^{-3} and 1.57×10^{-3} s^{-1} g_{metal}^{-1}, respectively. The turnover frequency (TOF), defined as the rate of converted isomaltulose (mol s^{-1}) per total mole of active metal species ($mole_{metal}$) (Ru in this case), for 5% and 10% Ru/C catalysts were also very similar, i.e. 1.36×10^{-2} and 1.32×10^{-2} $mol_{isomaltulose}$ s^{-1} mol_{Ru}^{-1}, respectively. Thus, it could be concluded that the turnover frequency did not depend on metal loading, and the catalyst with lower metal loading, i.e. 5wt%, would have a similar metal reduction degree with that with higher metal loaded catalyst, i.e. 10wt%. This virtually means that there was no other transport barrier for the metal to move about near the surface of the catalyst.

4.2.3 Effect of amount of catalyst

The effect of variation of amount of catalyst on conversion was investigated in this section. The reactions were performed under the condition specified in Table 4.5 except that the volume of isomaltulose was fixed at 83 ml and the amount of catalyst was set at 0.5 and 1.2 g. As shown in Figure 4.8, an increasing amount of catalyst could enhance the conversion of isomaltulose. In addition, the time to achieve a complete conversion decreased from 5 to 3 h. The turnover frequency at 1 h of the experiments with 0.5 and 1.2 g catalyst were 7.37×10^{-3} and 8.03×10^{-3} $mol_{isomaltulose}$ s^{-1} mol_{Ru}^{-1}, respectively and the reaction rate constant (*k*) for isomaltulose hydrogenation over 5%Ru/C and 10%Ru/C remained quite constant, i.e. 1.43×10^{-3} and 1.43×10^{-3} s^{-1} g_{metal}^{-1}, respectively. The ratio of weight catalyst in Table 4.7 was increased with increasing amount of catalyst because the volume of isomaltulose was constant. Moreover, the rate of reaction (*r*) increased with increasing amount of catalyst and this suggested a first order nature. This was not uncommon as more catalyst allowed easier matching between the reactant and the active site which enhanced the reaction rate.

Table 4.7 Effect of ratio of weight catalyst at temperature120°C, pressure 50 bar on 10%Ru/C

Condition	Amount of catalyst (g)	
	0.5	**1.2**
Volume of isomaltulose solution (ml)	83	83
Head space of reactor (ml)	134	134
Ratio of weight catalyst (g ml^{-1})	5.96×10^{-3}	14.31×10^{-3}
Ratio of weight Ru (g ml^{-1})	6.02×10^{-4}	1.45×10^{-3}
TOF (mol$_{\text{isomaltulose}}$ s^{-1} mol$_{\text{Ru}}$$^{-1}$)	7.37×10^{-3}	8.03×10^{-3}
Initial rate of reaction[a] (mol l^{-1} s^{-1})	6.52×10^{-5}	1.69×10^{-4}
k[b] (s^{-1} g$_{\text{metal}}$$^{-1}$)	1.43×10^{-3}	1.43×10^{-3}
Isomalt completion time (h)	5	3

[a] Initial rate of reaction from Equation 4.2

[b] Kinetic constant (*k*) from Equation 4.3

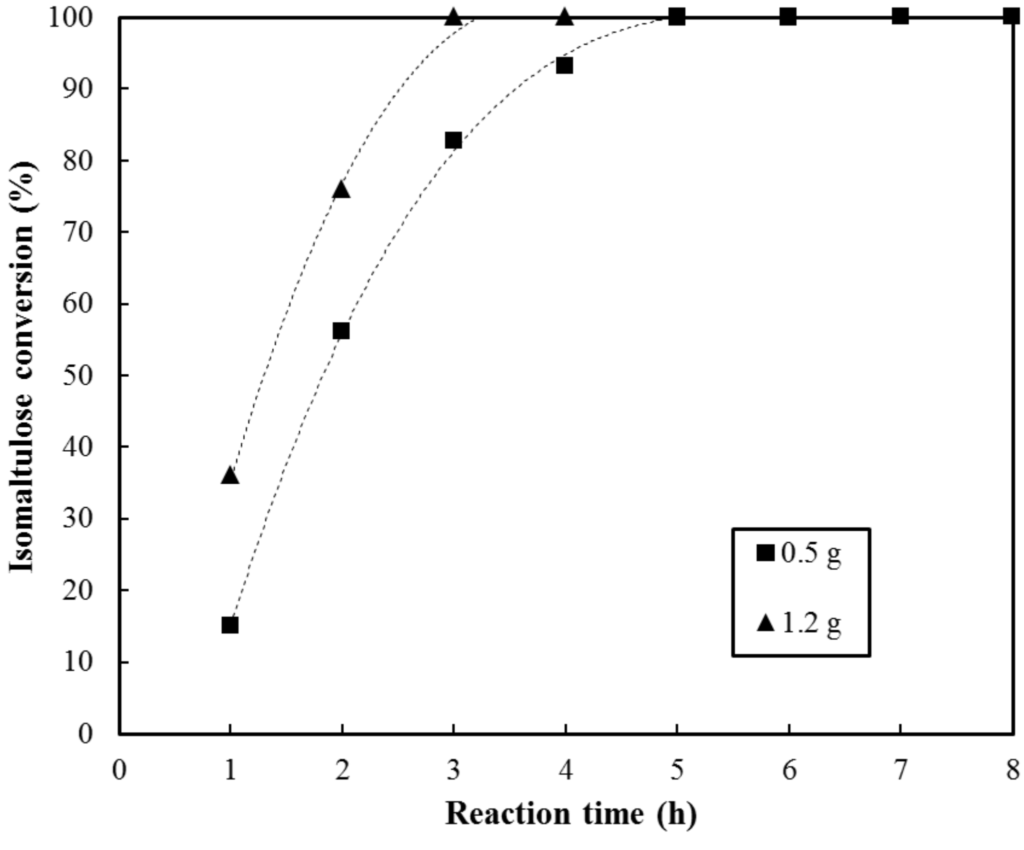


Figure 4.10 Effect of catalyst weight in the hydrogenation of isomaltulose on 10%Ru/C. Standard condition except the volume of isomaltulose is 83 ml

4.2.4 Effect of H_2 on hydrogenation

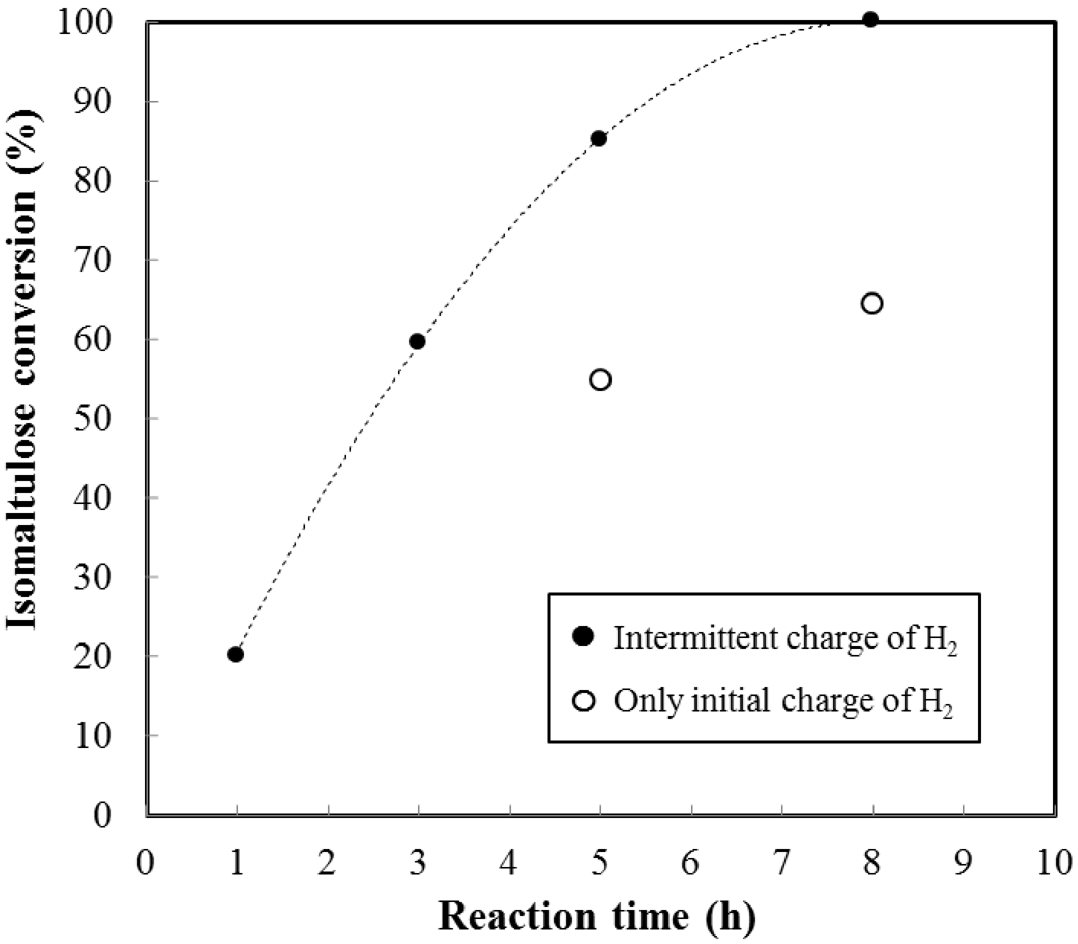


Figure 4.11 Effect of intermittent charge and only initial charge of hydrogen on hydrogenation of isomaltulose with 10%Ru/C, catalyst ratio of 3.58×10^{-3} g ml^{-1}, 50 bar, 120 °C, 40 wt% isomaltulose solution (139 ml)

Typical experiments started with the charging of H_2 at the beginning of the batch experiment where H_2 was consumed steadily until the end of reaction. This resulted in the reducing amount of H_2 throughout the reaction period. To maintain the amount of H_2 in the reaction, the experiment was adapted such that H_2 was recharged back to the starting pressure (i.e. 50 bar) into the reactor during the sampling periods (1-3 hours). The results of such operation are illustrated in Figure 4.9 where the dashed line with dark filled circles (--●--) represents results from the intermittent charged H_2 operation and the unfilled circles are for the typical experiment where H_2 was only initially charged into the reactor at the beginning of the operation. The isomaltulose conversion of 85% at 5 h could be obtained from the intermittent charged operation and the reaction could be completed within 8 h. On the other hand, the only initially charged operation could only see a much less isomaltulose conversion, c.a. 55 and 62% at 5 and 8 h, respectively. This emphasized the significance of H_2 on the reaction rate.

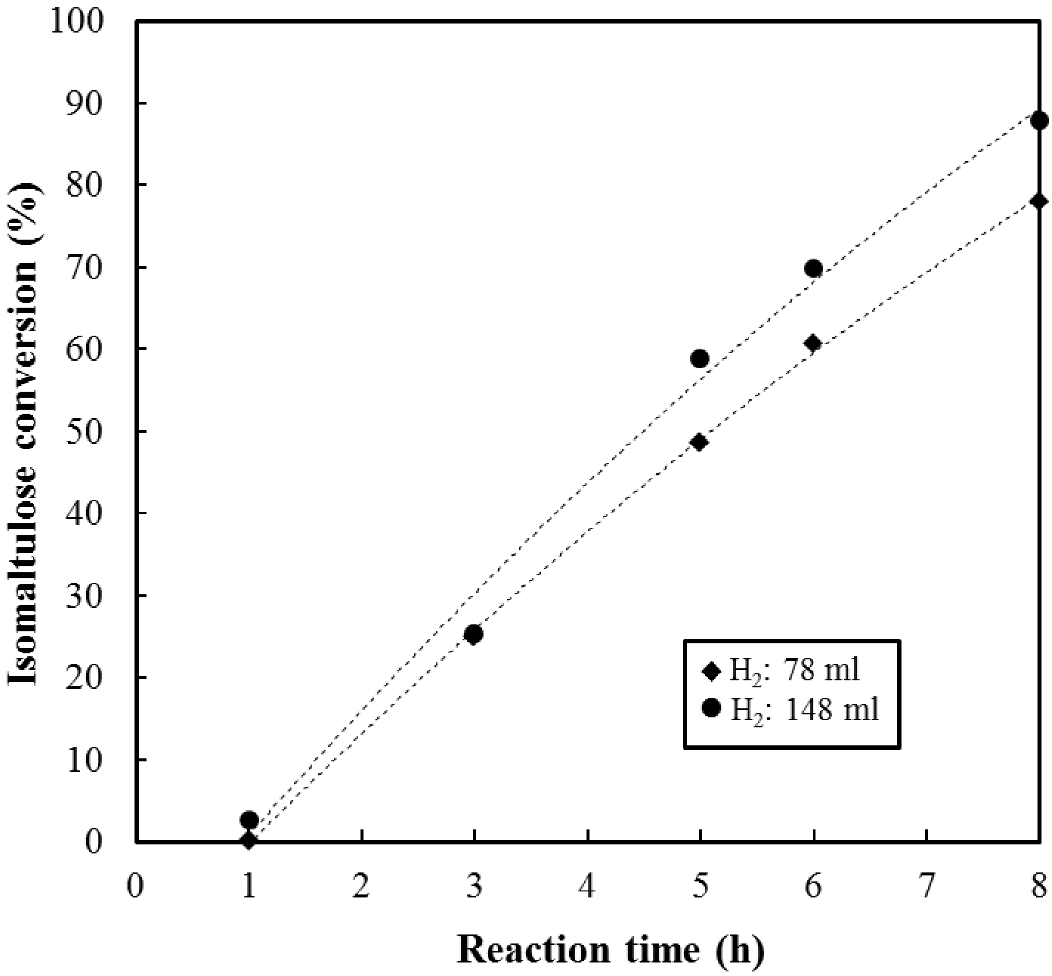


Figure 4.12 Effect of hydrogen on hydrogenation of isomaltulose with 10%Ru/C, catalyst ratio of 3.58×10^{-3} g ml^{-1}, 40 bar, 120 °C, 40 wt% isomaltulose solution

Table 4.8 Effect of amount of H_2 at reaction pressure of 40 bar, temperature of 120 °C

	Volume of hydrogen (ml)	
	78	148
Starting mole of isomaltulose (mol)	0.10	0.12
Starting mole of Hydrogen (mol)	0.12	0.24
Volume of isomaltulose (ml)	139	69
Ratio of weight catalyst (g ml^{-1})	3.60×10^{-3}	7.25×10^{-3}
Ratio of weight Ru (g ml^{-1})	3.60×10^{-4}	7.25×10^{-4}
H_2:isomaltulose ratio[a] (at start)	1.2	2
Initial rate of reaction[b] (mol l^{-1} s^{-1})	5.64×10^{-5}	6.71×10^{-5}
TOF (mol$_{\text{isomaltulose}}$ s^{-1} mol$_{\text{Ru}}^{-1}$)	5.73×10^{-2}	6.82×10^{-2}
Rate constant, k[c] (s^{-1} g$_{\text{metal}}^{-1}$)	1.02×10^{-3}	1.11×10^{-3}

[a] H_2:isomaltulose ratio = mole of Hydrogen (mol)/ mole of isomaltulose (mol)
[b] Initial rate of reaction from Equation 4.2
[c] Kinetic constant (k) from Equation 4.3

The effect of amount of H_2 on isomaltulose conversion was investigated further by varying the head space volume over isomaltulose solution, i.e. 78 and 148 ml with constant H_2 pressure (Figure 4.10). These corresponded to the isomaltulose solution of 139 and 69 ml, respectively. It was assumed that H_2 solubility was similar for all cases which were the equilibrium concentration at 40 bar. As shown in Figure 4.10, although the amount of H_2 was almost double, the increase of isomaltulose conversion was small and considered insignificant. In this case, as the amounts of H_2:isomaltulose were both in excess (as shown in Table 4.8) as one mole of isomaltulose only requires half a mole of H_2 for its complete hydrogenation. This suggested that H_2 needed for the reaction had to be in soluble form and H_2 fed into the head space of the reactor would need to dissolve into the solution before reacting with the sugar. The amount of dissolved H_2 in the solution depends on the imposed pressure, but not on the volume of the head space. Therefore the experiments with large H_2 volume could not lead to an improved hydrogenation performance, unlike the previous experiment where H_2 was continually intermittent charged into the system at 50 bar which could maintain the dissolved H_2 at an adequately high level for the reaction to complete.

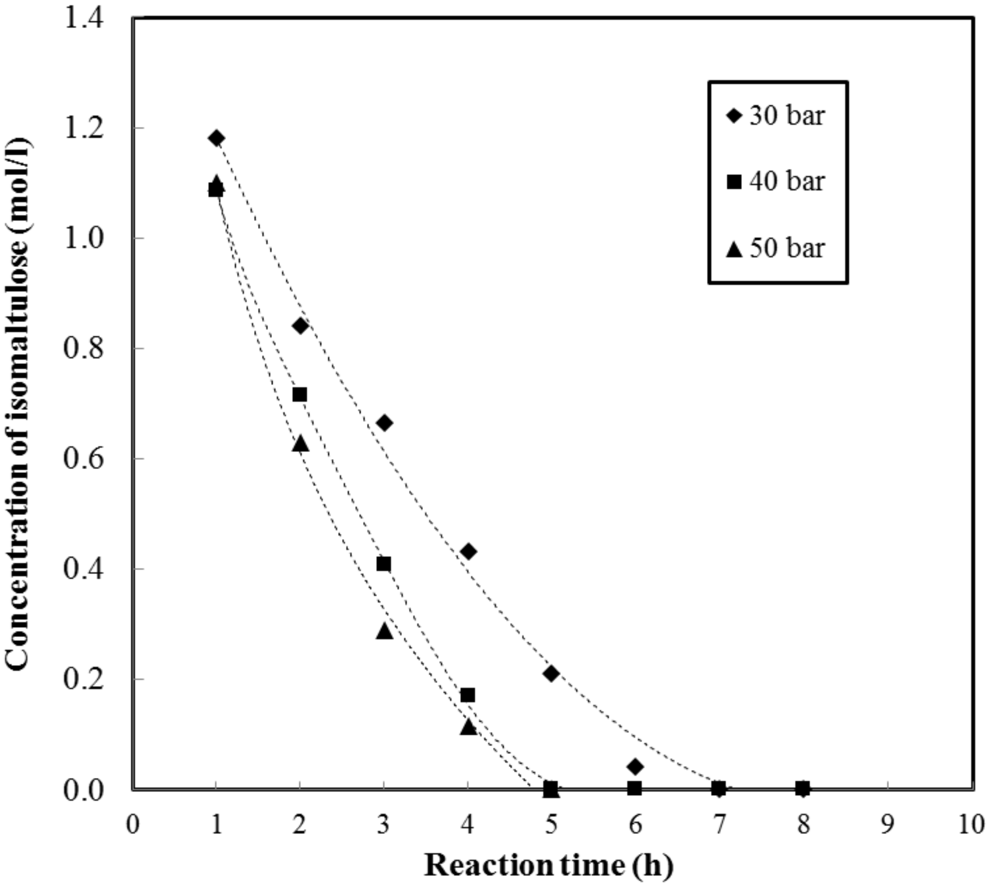


Figure 4.13 Influence of hydrogenation pressure on concentration of isomaltulose

Table 4.9 Effect of H_2 pressure on hydrogenation at temperature 120 °C

Initial setting	Pressure(bar)		
	30	40	50
mole of isomaltulose (mol)	0.13	0.12	0.10
mole of Hydrogen (mol)	0.16	0.21	0.27
Volume of isomaltulose (ml)	83	83	83
Ratio of weight catalyst (g ml^{-1})	6.02×10^{-3}	6.02×10^{-3}	6.02×10^{-3}
Ratio of weight Ru (g ml^{-1})	6.02×10^{-4}	6.02×10^{-4}	6.02×10^{-4}
H_2:isomaltulose ratio[a]	1.24	1.78	2.67
Initial rate of reaction[b] (mol l^{-1} s^{-1})	9.42×10^{-5}	1.12×10^{-4}	1.42×10^{-4}
TOF ($mol_{isomaltulose}$ s^{-1} mol_{Ru}^{-1})	1.32×10^{-2}	1.71×10^{-2}	1.79×10^{-2}
Rate constant, k^c (s^{-1} g_{metal}^{-1})	2.07×10^{-3}	2.59×10^{-3}	2.62×10^{-3}

[a] H_2:isomaltulose ratio = mole of Hydrogen (mol)/ mole of isomaltulose (mol)
[b] Initial rate of reaction from Equation 4.2
[c] Kinetic constant (*k*) from Equation 4.3

To prove this, the reactions were carried out with varying initial H_2 pressure. Figure 4.11 illustrates that the reaction could be enhanced with increasing H_2 pressure from 30 to 40 and 50 bar. The initial rates of reaction and the turnover frequency within the first hour are calculated as shown in Table 4.9. Similar tendency of reaction pressure on the reaction performance were observed as the reaction rate increased with increasing H_2 pressure up to 50 bar. An increasing H_2 pressure could increase H_2 solubility in the liquid and led to an increasing available H_2 concentration for the reaction. Note that, due to the limitation of the experimental device, it was not possible to investigate the system performance at the pressure above 50 bar.

Although the solubility of H_2 might explain the on-going phenomena quite reasonably, there might also be a chance that the reaction was controlled by the surface adsorption of H_2 onto the catalyst surface which might increase with the applied pressure. This issue will need to be investigated further.

4.2.5 Effect of reaction temperature on hydrogenation

The effect of the reaction temperature, i.e. 100, 120 and 130°C on the hydrogenation of isomaltulose is displayed in Figure 4.12. The reactions were performed under the condition in Table 4.5 except that the volume of isomaltulose solution was 83 ml. Isomaltulose conversion dramatically increased with increasing reaction temperature from 100 to 120°C and could be further increased with a temperature of 130°C.

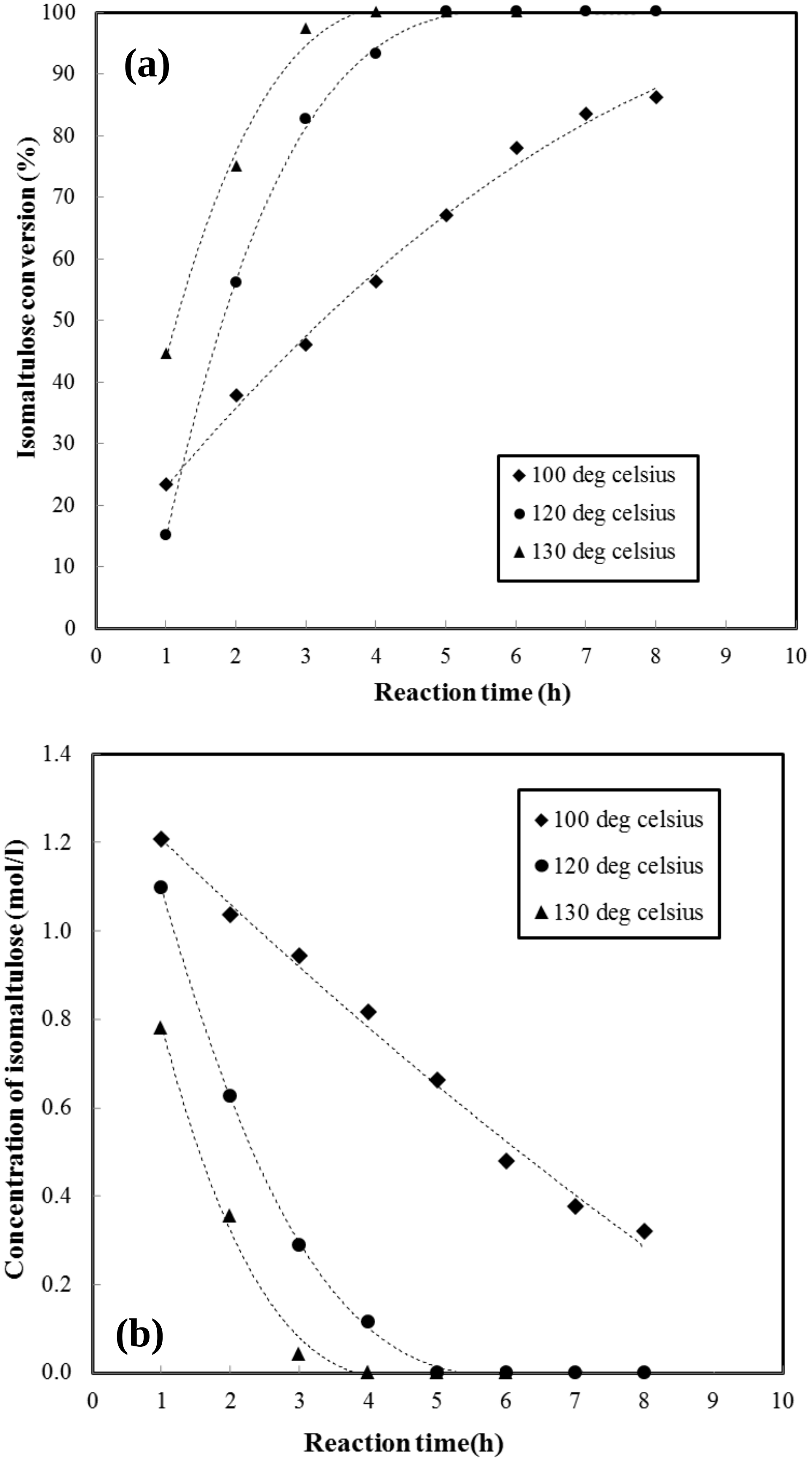


Figure 4.14 Influence of hydrogenation temperature on (a) isomaltulose of conversion (%) (b) concentration of isomaltulose (mol l^{-1})

Table 4.10 Effect of temperature on hydrogenation at initial pressure 50 bar

Initial setting	Temperature(°C)		
	100	120	130
mole of isomaltulose (mol)	0.10	0.08	0.06
mole of H_2 (mol)	0.27	0.27	0.27
Volume of isomaltulose (ml)	83	83	83
Ratio of weight catalyst (g ml^{-1})	6.02×10^{-3}	6.02×10^{-3}	6.02×10^{-3}
Ratio of weight Ru (g ml^{-1})	6.02×10^{-4}	6.02×10^{-4}	6.02×10^{-4}
H_2:isomaltulose molar ratio[a]	2.70	3.38	4.50
Initial rate of reaction[b] (mol l^{-1} s^{-1})	4.13×10^{-5}	1.42×10^{-4}	1.48×10^{-4}
TOF ($mol_{isomaltulose}$ s^{-1} mol_{Ru}^{-1})	1.17×10^{-2}	1.79×10^{-2}	3.44×10^{-2}
Rate constant, k^c (s^{-1} g_{metal}^{-1})	8.15×10^{-4}	2.43×10^{-3}	3.80×10^{-3}

[a] H_2:isomaltulose ratio = mole of Hydrogen (mol)/ mole of isomaltulose (mol)

[b] Initial rate of reaction from Equation 4.2

[c] Kinetic constant (*k*) from Equation 4.3

Figure 4.12 illustrates that isomaltulose could be completely converted to isomalt within 4 and 5 h at the reaction temperature of 130 and 120 °C, respectively. The conversion at 100 °C could not be completed at 8 h (86.1 %isomaltulose conversion). Hence, the increased hydrogenation temperature in the range from 110 to 130 °C clearly improved the reaction rate. Elevated reaction temperature increased the turnover frequency, rate constant (*k*) of reaction, and solubility of hydrogen.

The adsorption constant of hydrogen from Equation (4.6) varied between 1.97 and 2.51 bar^{-1} depending on temperature (100-130°C). The heat of adsorption of hydrogen was estimated to be 12 kJ mol^{-1} (Equation (4.4). From the Arrhenius plot (Figure 4.17) of the initial rates measured in the range 100, 120 and 130 °C under 50 bar (Figure 4.16), the observed activation energy (E_a) of about 64.67 kJ mol^{-1} was obtained. This value, much larger than the activation energy of diffusion in liquids (12-21 kJ mol^{-1} (Dechamp et al., 1995), indicates that the reaction rate might be controlled by the kinetics on the metal surface. The result in this study demonstrated that the temperature had effects on isomaltulose hydrogenation.

4.3 Stability of 10%Ru/C catalyst for hydrogenation of isomaltulose

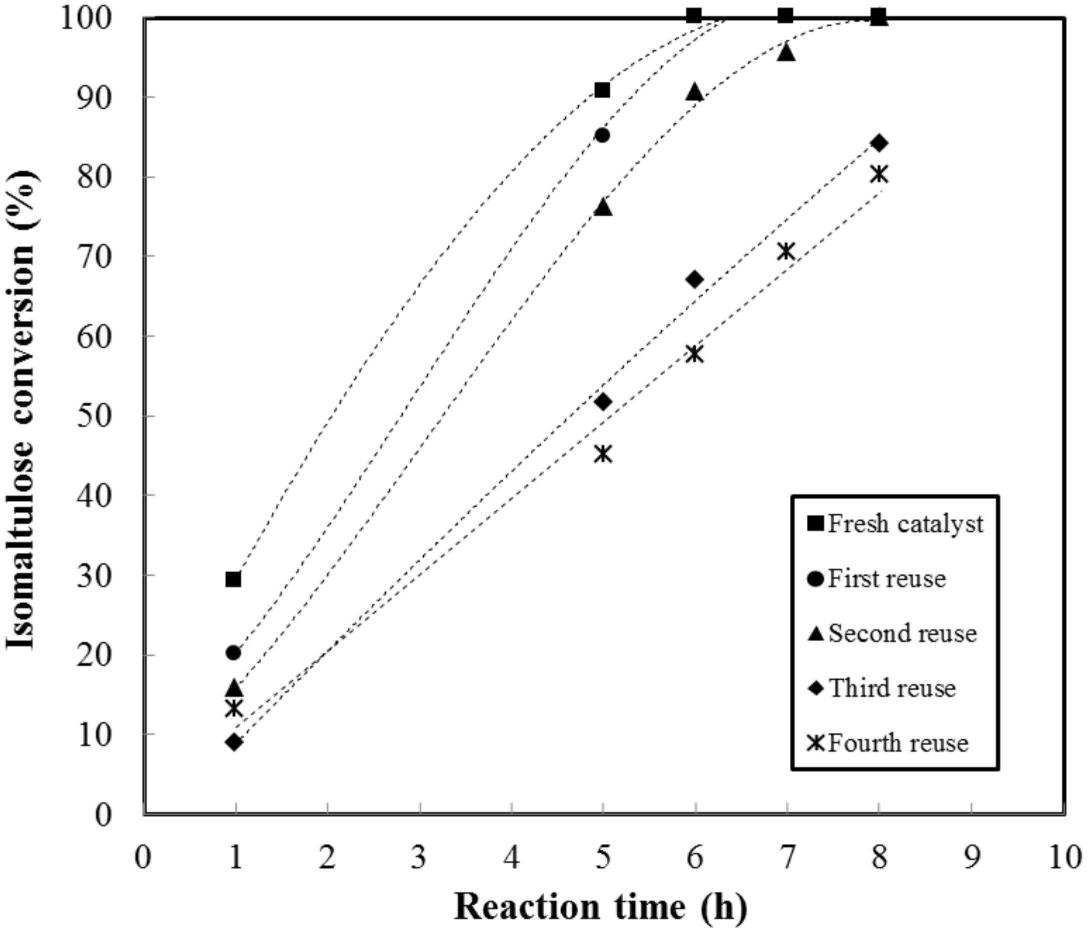


Figure 4.15 Performance of reused catalyst on hydrogenation of 40 wt% isomaltulose solution with 0.5 g 10%Ru/C catalyst at 50 bar and 120°C

As shown in Figure 4.13, isomaltulose conversion decreased with an increasing number of reuse cycles. The elemental analysis (Table 4.8) reveals that Ru content decreased as the catalyst was being reused. In addition, considering the rate constant (*k*) as summarized in Table 4.8, it was observed that *k* which was based on the active metal content of fresh, the 1st and 2nd reuses, although slightly, continually decreased. This indicates that there were two reasons responsible for this loss. The first one is the leaching of Ru from the activated carbon support and the other one is the loss in the activity of the catalyst itself as described below.

Table 4.8 Ru content of fresh and reused catalysts and corresponding reaction rate constants

Catalysts	Fresh catalyst	First reuse	Second reuse	Third reuse	Forth reuse
Ru loading[a] (wt%)	12.2	10.9	9.6	9.6	n.a.
k^b ($s^{-1}\,g_{Ru}^{-1}$)	1.68×10^{-3}	1.37×10^{-3}	1.31×10^{-3}	1.17×10^{-3}	1.13×10^{-3}
Weight catalyst (g)	0.5	0.4557	0.4504	0.4401	0.4364
Weight loss	-	0.0443	0.0496	0.0599	0.0636
% Weight loss	-	8.86	9.92	11.98	12.72
Reduction in k ($s^{-1}\,g_{Ru}^{-1}$)	-	3.10×10^{-4}	3.70×10^{-4}	5.10×10^{-4}	5.50×10^{-4}
% reduction in k	-	18.45	22.02	30.36	32.74

[a] measured with X-ray fluorescence spectrometer

[b] Kinetic constant (*k*) from Equation 4.3

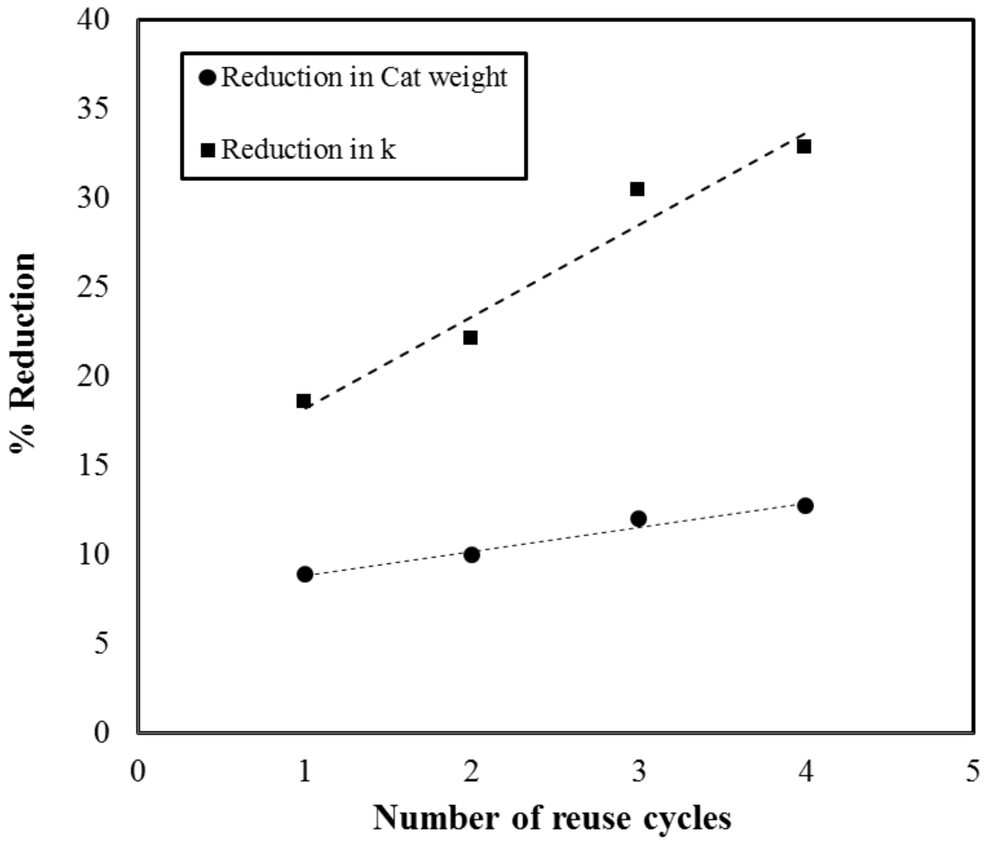


Figure 4.16 Relationship between %reduction in catalyst weight and %reduction in rate constant (*k*)

The leaching of catalyst from the support was responsible for on part of the losses of the activity. Figure 4.14 demonstrates that, apart from leaching, the catalyst activity (k) also decreased, even in a greater extent than the leaching loss. This activity loss could potentially occur due to the oxidation of the active site (Ruthenium to ruthenium dioxide) which no longer catalyzed this hydrogenation reaction. Although this was not proven in this present work, it was proposed as one of the potential causes of catalyst deactivation here.

4.4 Kinetic parameters determination

The hydrogenation of isomaltulose is assumed to follow the following pathway:

$$2C_{12}H_{22}O_{11} \quad + \quad H_2 \quad \longrightarrow 2C_{12}H_{23}O_{11} \tag{4.1}$$

As the reactor was designed to be perfectly stirred, the batch-reactor model could be used and the design equation can be derived as:

$$-\frac{dC_{isomaltulose}}{dt} = \frac{dC_{isomalt}}{dt} = w_{catalyst} r_i \tag{4.2}$$

where $C_{Isomaltulose}$ is the isomaltulose concentration (mol l^{-1}), $C_{Isomalt}$ is the isomalt concentration (mol l^{-1}), $w_{catalyst}$ is the weight of metal in catalyst (g_{metal}) and r_i is rate of reaction (mol l^{-1} s^{-1}).

Although the effect of hydrogen was suspected to be due to its dissolved concentration in the solution, it was assumed here that this dissolved concentration varied linearly with the pressure (as hydrogen is a sparingly soluble gas). At the hydrogen pressure of 30, 40 and 50 bar, the reaction rate increased linearly with an increase in hydrogen pressure (Figure 4.15), indicating the first order behavior with respect to hydrogen.

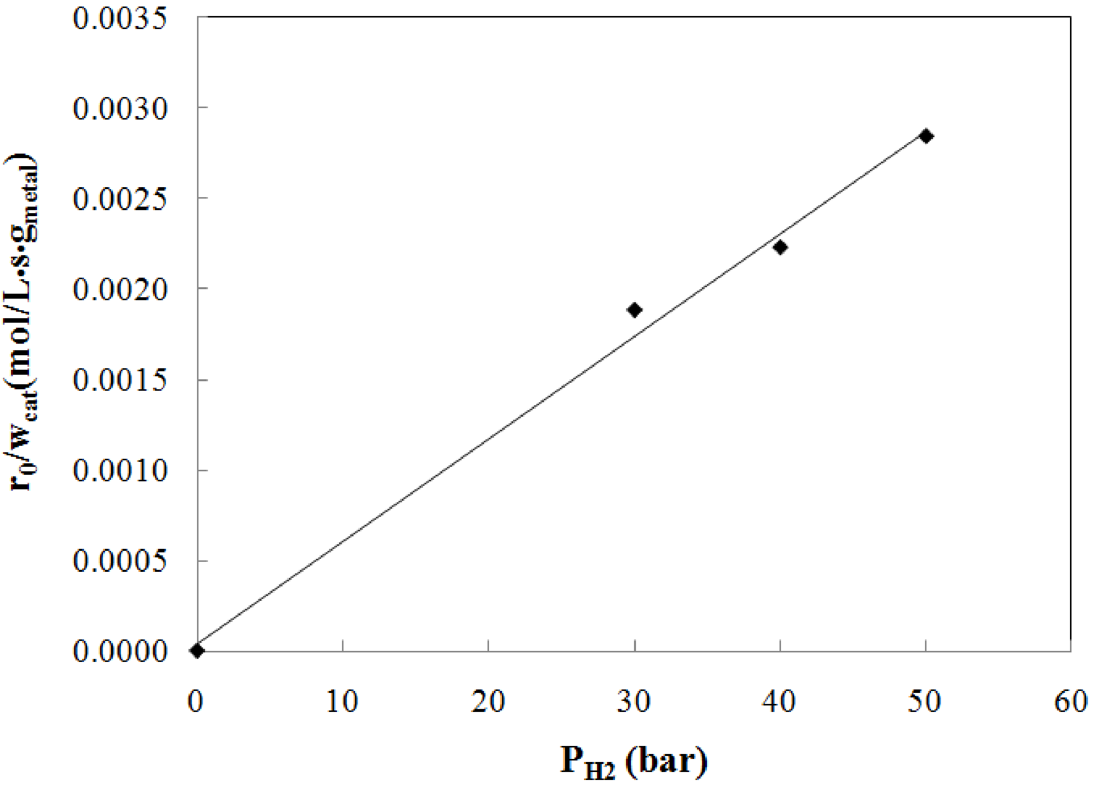


Fig. 4.17 Normalized initial isomaltulose hydrogenation rate as a function of hydrogen pressure at 393 K and w_{cat} = 0.05 g

The kinetic data were modeled using Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic assuming that the surface reaction was rate determining. The kinetic model involved non competitive adsorption of hydrogen and isomaltulose (Equation 4.3).

$$-r_{\text{isomaltulose}} = \frac{kC^{n}_{\text{isomaltulose}} P^{m}_{\text{H}_2} K_{\text{H}_2} K_{isomaltolose}}{(1+K_{\text{H}_2} P^{m}_{\text{H}_2})(1+K_{\text{isomaltulose}} C^{n}_{\text{isomaltulose}})} \qquad (4.3)$$

where $C_{\text{Isomaltulose}}$, P_{H2}, K_{H2}, $K_{\text{isomaltulose}}$, k and (n, m) represent, respectively, the isomaltulose concentration (mol l^{-1}), hydrogen gas pressure (bar), adsorption constants of hydrogen (bar^{-1}), adsorption constants of isomaltulose (mol l^{-1}) kinetic constants (s^{-1} $g_{\text{metal}}{}^{-1}$) and orders of reaction. The order of reaction was determined with the optimization solver provided in the widely available commercial spreadsheet software (like MS Office 2007). In addition, the adsorption constants K_{H2} and $K_{isomaltulose}$ were presumed to be independent of temperature and calculated from Equations 4.4 – 4.5.

$$K_{H_2} = \exp\left(\frac{-\Delta H_H}{RT}\right) \tag{4.4}$$

$$K_{isomaltulose} = \exp\left(\frac{-\Delta H_{isomaltulose}}{RT}\right) \tag{4.5}$$

where ΔH_H is heat of adsorption of hydrogen (kJ mol^{-1}) and $\Delta H_{isomaltulose}$ is heat of adsorption of isomaltulose (kJ mol^{-1}). Equation 4.4 and Van't Hoff plot can be transformed to:

$$K_{H_2} = 0.21\exp\left(\frac{12000}{RT}\right) \tag{4.6}$$

The regressed temperature-dependent rate constants according to the Arrhenius' equation are illustrated in Figures 4.16 and 4.18. The sorption equilibrium constant of hydrogen as a function of temperature was determined by the Van't Hoff plot as shown in Figure 4.16. The sorption equilibrium of hydrogen was found to decrease with temperature as regularly observed in most adsorption processes. The heat of adsorption of hydrogen (ΔH_H) calculated by Equation (4.4) was 12 kJ mol^{-1}, which was in the range of the previously reported values of 19.3±11 kJ mol^{-1} (Mun et al., 2007).

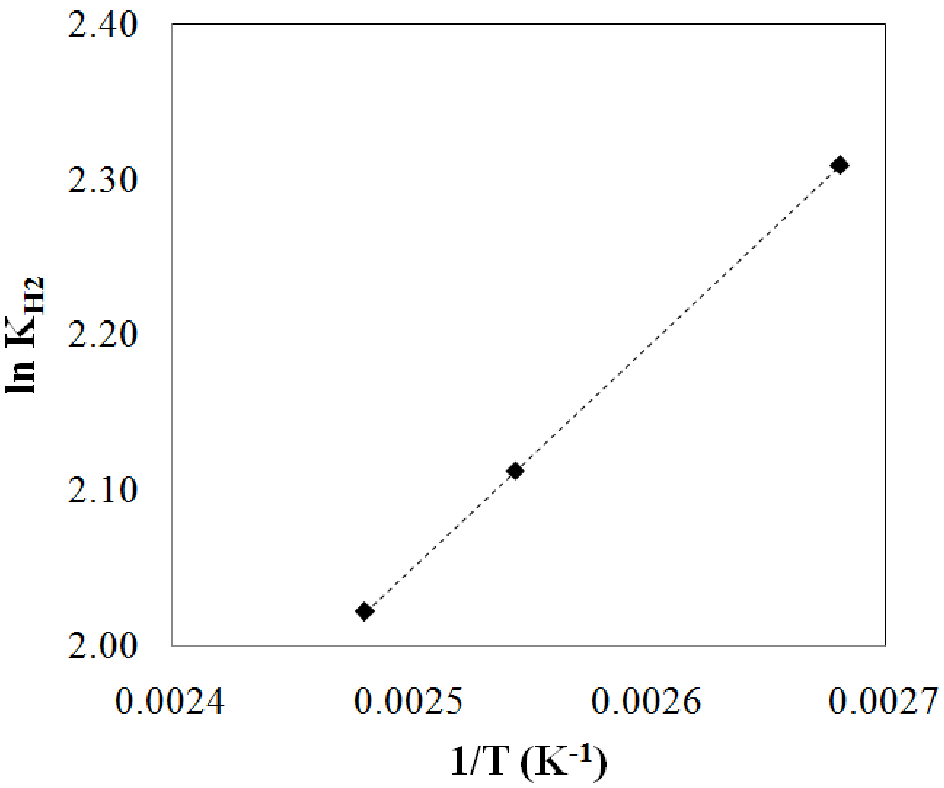


Figure 4.18 Van't Hoff plot

Since hydrogen molecules are much smaller than isomaltulose molecules, interstitial sites between adsorbed isomaltulose molecules were assumed to remain accessible for hydrogen adsorption. Thus the adsorption behavior shifted towards a non-competetive one. Equation 4.3 can then be transformed to:

$$-r_{isomaltulose} = \frac{kK_{H_2}C^{n}{}_{isomaltulose}P^{m}{}_{H_2}}{(1+K_{H_2}P^{m}_{H2})} \tag{4.7}$$

Results of a kinetic experiment are presented in Figure 4.19. Provided m = 1 from the correlation as shown in Figure 4.15, experimental data could be employed to estimate these kinetic parameters. The parameters estimation was carried out using experimental data from the operations at various pressures and temperatures. The parameter of the main reaction were well identified using the excel optimization solver tool and the results are shown in Table 4.9. This demonstrates that the reaction rate constant was a function of temperature following the Arrhenius correlation as shown in Figure 4.18. The coefficient of determination for the kinetic tested are calculated from Equation 4.7 (Appendix G). A good deterministic model describing the reaction kinetic should have a high coefficient of determination (Sifontes et al., 2010).

Table 4.9 Kinetic parameters

Condition		Parameter		
Temperature (^{o}C)	Pressure (bar)	K_{H2}(bar^{-1})	N	k(s^{-1} g$_{metal}$$^{-1}$)
120	30	2.13	1	2.41×10^{-3}
120	40	2.13	1	2.59×10^{-3}
120	50	2.13	1	2.62×10^{-3}
100	50	2.51	1	8.12×10^{-4}
130	50	1.97	1	3.80×10^{-3}

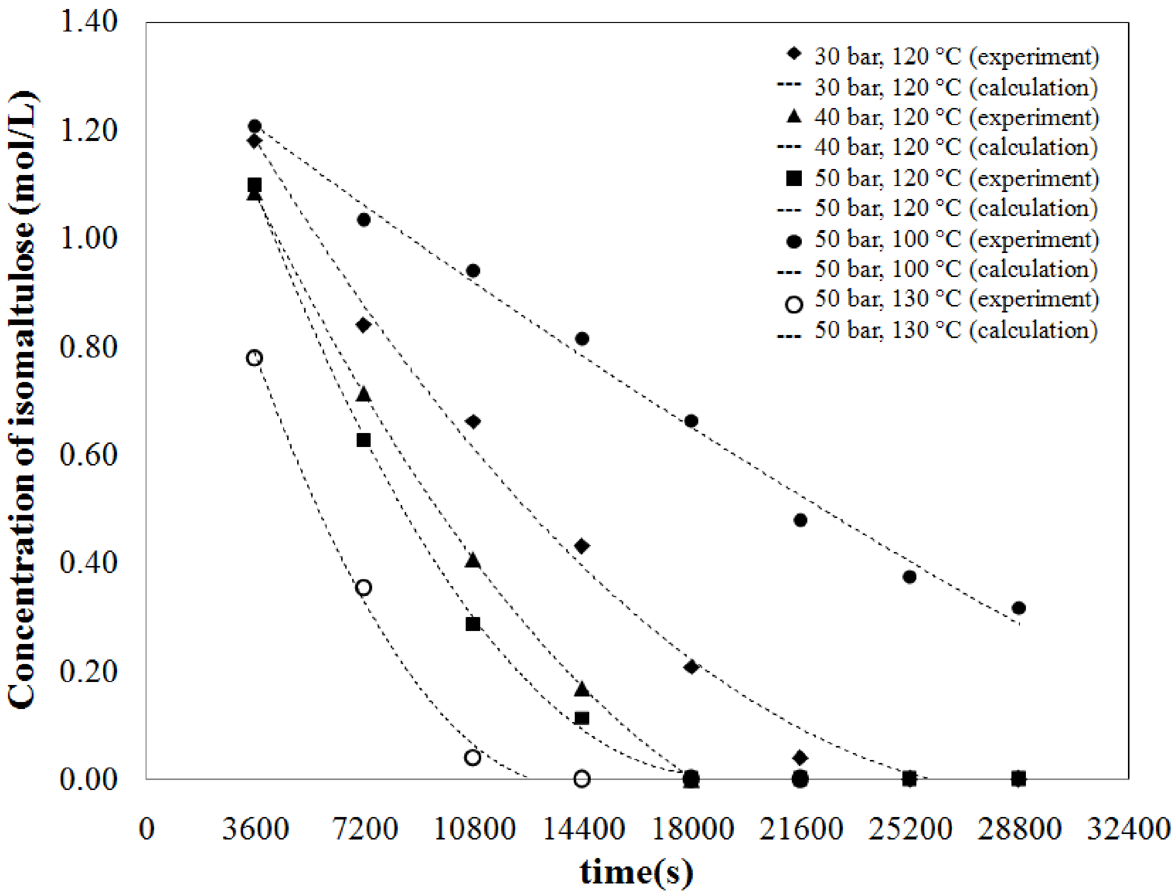


Figure 4.19 Model trend line for hydrogenation of isomaltulose

$$R^2 = \left(1 - \frac{\sum_{i=1}^{n}\left(C_{\mathrm{exp}erimental_i} - C_{calculation_i}\right)^2}{\sum_{i=1}^{n}\left(C_{\mathrm{exp}erimental_i} - C_{mean}\right)^2}\right) \times 100\% \qquad (4.7)$$

where $C_{\mathrm{experimental}}$ = concentration of isomaltulose from experiment (mol l^{-1}), $C_{\mathrm{calculation}}$ = concentration of isomaltulose from calculation (mol l^{-1}) and C_{mean} = the mean concentration of isomaltulose from experiment (mol l^{-1})

Table 4.10 Effect of temperature on isomaltulose hydrogenation at standard condition

Temperature (^{o}C)	k(s^{-1} g_{metal}^{-1})	1/T (K^{-1})	ln(k)
100	8.12×10^{-4}	0.002681	-7.11629
120	2.62×10^{-3}	0.002545	-6.01986
130	3.80×10^{-3}	0.002481	-5.57375

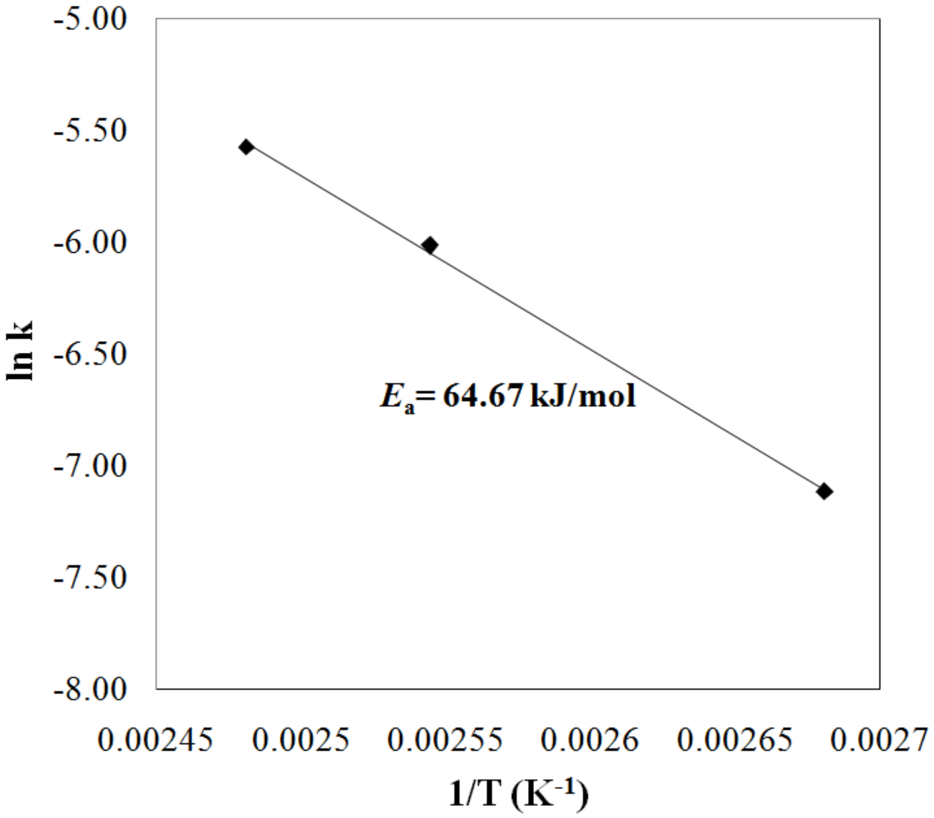


Figure 4.20 Arrhenius plot for hydrogenation of 40 wt% aqueous solution of isomaltulose at 50 bar, 10%Ru/C 0.5 g

The activation energy was calculated from the Arrhenius equation which can be written as follows:

$$k = Ae^{\left(-Ea/_{RT}\right)} \tag{4.8}$$

where A = exponential factor, E_a = activation energy (kJ mol^{-1}), T = temperature (K) and R = gas constant (8.3145 mol^{-1} K^{-1}). The Arrhenius plot of ln(k) versus 1/T are shown in Figure 4.16.

Table 4.10 shows the kinetic parameters using the initial isomaltulose concentration $C_{isomaltulose}$ = 40% (1.39 mol l^{-1}) and the catalyst amount of 0.5 g, at various hydrogen (H_2) pressures of 30, 40 and 50 bar at 120 °C, and also at various temperatures of 100, 120 and 130°C at the fixed hydrogen pressure of 50 bar. The first order reaction rate constant (k) increased with an increasing reaction temperature, whereas the adsorption constant of hydrogen (K_{H2}) (Equation 4.6) took the opposite trend. The correlation was relatively good with an R^2 of 98% (Equation 4.7). The model trend line in Figure 4.17 indicates that the proposed model nicely describes the behavior of the system. It was found that the activation energy for isomaltulose hydrogenation over Ru/C was 64.67 kJ mol^{-1} (Figure 4.18).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The hydrogenation of isomaltulose was successfully performed with an activated charcoal supported ruthenium catalyst (Ru/C) in a pressure vessel stirring reactor. With proper operating conditions, e.g. high hydrogen pressure and high temperature, Isomaltulose can be converted to isomalt at 100% conversion. The most optimal preparation conditions for the catalyst are summarized in Table 5.1. Kinetic data were obtained under condition in which intrinsic kinetic prevailed (stirring speed = 670 rpm, 10%Ru/C catalyst, and initial sugar concentration = 40%). The rate of reaction was first order with respect to hydrogen. Furthermore, the reaction rate constant (k) depended on reaction temperature, and the adsorption constant of hydrogen (K_{H2}) decreased with an increasing reaction temperature. The observed activation energy was 64.67 kJ mol^{-1}. Kinetic parameters were estimated for all experimental conditions and are summarized in Table 5.2.

Table 5.1 The most optimal preparation conditions for the catalyst

Property	**Value**
Catalyst	Ruthenium over charcoal activated carbon
Catalyst synthesis method	Dry impregnation
Surface area	665 m^2 g^{-1}
Ruthenium content	10%(w/w)
Particle average size	2-4 nm
Calcination gas and temperature	Argon (500 °C)
Reducing gas and temperature	Hydrogen (200 °C)

Table 5.2 Kinetic parameter estimation

Condition	$-r_{isomaltulose} = \frac{kK_{H_2}C^1_{isomaltulose}P^1_{H_2}}{(1+K_{H_2}P^1_{H2})}$		
	k(s^{-1} g$_{metal}$$^{-1}$)	K_{H2}(bar^{-1})	R^2(%)
Temperature 120 ^{o}C, Pressure 30 bar	2.41×10^{-3}	2.13	97
Temperature 120 ^{o}C, Pressure 40 bar	2.59×10^{-3}	2.13	98
Temperature 120 ^{o}C, Pressure 50 bar	2.62×10^{-3}	2.51	98
Temperature 100 ^{o}C, Pressure 50 bar	8.12×10^{-4}	2.13	98
Temperature 130 ^{o}C, Pressure 50 bar	3.80×10^{-3}	1.97	97

5.2 Contributions

Isomalt has long been known as a special sugar converted from natural raw material. However, the production of such sugar is still not common particularly in the South East Asia region. This work provided some insight into how to produce this special sugar where details of the laboratory-scale technique are given. It was shown that the reaction takes place best at high hydrogen pressure and temperature. A milder condition could be employed to lower the operating cost but at the cost of lower yield. The choice of operating cost therefore depends on the economics of such options. The findings from this work, hence, can be a good starting point for the upscale work to pilot of industrial scale.

5.3 Recommendations

1. Due to experimental limitation, there are still certain parameters that should be visited for the hydrogenation of isomaltulose, e.g. feed concentration or initial sugar concentration, and type of metal loading on catalyst. This should be examined further.

2. Mass transfer in the reactor seemed to have important influence on the reaction kinetics. Therefore the design of proper reactors for this reaction may help optimize the production of such sugar.

3. How to help improve the stability of the catalyst is also interesting as it will extend the service time of the catalyst which can take a major part in controlling the operating costs.

4. This work has not looked into the various types of isomalt produced from the reaction. As only GPS form of isomalt is useful to human, future work should look into this.

5. Last, but not least, the raw material used in this work is pure isomaltulose. However, enzyme reaction that gives isomaltulose may allow some other sugar to take place. The production of isomalt based on this impure sugar mixture should be examined as it will help reduce the resources needed to purify isomaltulose.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Precursor description for the preparation of Ru/C catalyst:

Ruthenium (III) nitrosyl nitrate solution

Formula: Ru(NO)(NO3)x (OH)y, x+y=3

Molecular weight: 318.10 g mol^{-1}

Purity: 1.5 wt% metal

Density: 1.07 g cm^{-3}

Support description for the preparation of Ru/C catalyst:

Charcoal activated powder

Formula: C

Density: 2.267 g cm^{-3}

Example of Calculation (dry impregnation):

Precursor: 10 wt% Ru of Ruthenium (III) nitrosyl nitrate solution $[Ru(NO)(NO_3)_x(OH)_y, x+y=3]$

Support: Carbon (C)

- Calculation for the preparation of 10%Ru/C catalyst with $Ru(NO)(NO_3)_x(OH)_y$, x+y=3 as Ru precursor

  Based on 100 g of catalyst used, the composition of the catalyst is as follows:

  Ru = 10 g

  C = 100-10 = 90 g

  For 2 g of catalyst

  Ru required = 2 × (10/90) = 0.22 g

Ruthenium 0.22 g was prepared from Ruthenium (III) nitrosyl nitrate solution.

- Molecular weight of Ruthenium metal = 101.07 g
- Molecular weight of Ruthenium (III) nitrosyl nitrate = 318.10 g

To obtain 0.22 g of ruthenium metal

- Ruthenium (III) nitrosyl nitrate required = 0.22 × (318.10 /101.07)

= 0.70 g

- Density of Ruthenium (III) nitrosyl nitrate solution= 1.07 g cm^{-3}
- Ruthenium (III) nitrosyl nitrate solution required = (0.70/1.07) = 0.65 ml

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

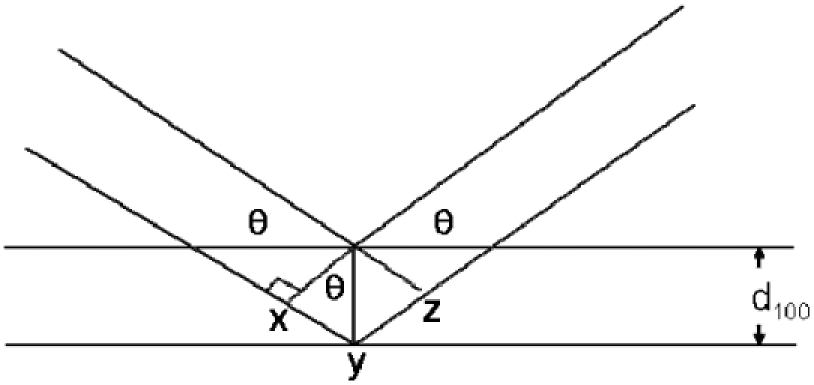

Figure B.1 Derivation of Bragg's Law for X-ray diffraction

$xy = yz = d\sin\theta$

Thus $xyz = 2d\sin\theta$

But $xyz = n\lambda$

Therefore $2d\sin\theta = n\lambda$

Bragg's Law $$D = \frac{K\lambda}{\beta\cos\theta} \qquad \text{(B.1)}$$

where D = Crystallite size, Å

K = Crystallite-shape factor = 0.9

λ = X-ray wavelength, 1.5418 Å for CuKα

θ = Observed peak angle, degree

β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of powder diffraction free from all broadening due to the experimental equipment. α-alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M^2 - B_S^2} \tag{B.2}$$

where BM = The measured peak width in radians at half peak height.

BS = The corresponding width of the standard material.

Example: Calculation of the crystallite size of Ruthenium metal of 10%Ru/C catalysts

The half-height width of 101 diffraction peak = 4.03° (from data of XRD)

$$= \frac{4.03\times\pi}{180} = 0.07025 \text{ radian}$$

The corresponding half- height width of peak of Ruthenium metal (from the B_s value at the 2θ of 44.87° from data of XRD) = 0.004459

The pure width, β $= \sqrt{B_M^2 - B_S^2}$

$= \sqrt{0.07025^2 - 0.004459^2}$

$=$ 0.0701 radian

β = 0.0701 radian

2θ = 44.87°

θ = 22.435°

λ = 1.5418 Å

$$\text{The crystallite size} = \frac{0.9\times1.5418}{0.0701\cos22.435} = 21.41\ \text{Å} = 2.14\ \text{nm}$$

APPENDIX C

CALCULATION OF ISOMALTULOSE CONVERSION, SELECTIVITY AND YIELD

% Conversion = $$\left(\frac{\text{Isomaltulose in - Isomaltulose out}}{\text{Isomaltulose out}}\right)\times 100\%$$

% Selectivity = $$\left(\frac{\text{Isomalt product}}{\text{sum of all products}}\right)\times 100\%$$

% Yield = $$\left(\frac{\text{\% Conversion}\times\text{\% Selectivity}}{100}\right)$$

APPENDIX D

SAMPLE OF CALCULATION

D1 Calculation of hydrogen consumed

The calculation of hydrogen consumed are as follow:

Let P = hydrogen consumed, psi

T = temperature during operation, K

V = volume of hydrogen stored tank, m^3

R = 8.31×10^{-5} m^3 bar mol^{-1} K^{-1}

n = mol of hydrogen

From ideal-gas equation

$PV = nRT$

$n = PV/RT$

(D.1)

At volume of H_2 is 7.8×10^{-5} m^3 at pressure 40 bar and temperature 303 K

$$n = \frac{40\times7.8\times10^{-5}}{8.31\times10^{-5}\times303}$$

n = 0.12 mol

D2 Calculation of isomaltulose consumed

The calculation of isomaltulose consumed is as follow:

From Eq.D.1 $n = PV/RT$

At volume of isomaltulose of 1.39×10^{-4} m^3, at 40 bar and 303 K

$$n = \frac{40\times1.39\times10^{-4}}{8.31\times10^{-5}\times303}$$

n = 0.22 mol

D3 Calculation of H_2:Isomaltulose ratio

The calculation of isomaltulose consumed is as follows:

Let H2 = hydrogen consumed, mol

Isomaltulose = isomaltulose consumed, mol

From H_2:Isomaltulose ratio equation

$$H_2\text{:Isomaltulose ratio} = \frac{\text{mol of hydrogen}}{\text{mol of isomaltulose}} \quad \text{(D.2)}$$

At volume of isomaltulose is 1.39×10^{-4} m^3 and volume of H_2 is 7.8×10^{-5} m^3 at pressure 40 bar and temperature 303 K

From Eq.D.2 H_2:Isomaltulose ratio $= \frac{0.12}{0.22}$

$= 0.6$

D4 Determination of the Activation Energy

From Arrhenius Equation:

$$k = A \exp(-E_a/RT)$$

In the logarithmic from:

$$\log k = \log A - E_a/RT$$

where k = the overall rate constant, min^{-1}

A = the frequency factor, min^{-1}

E_a = the activation energy, kJ mol^{-1}

R = the gas constant, 8.314 J mol^{-1} K^{-1}

T = absolute temperature, K

From Figure 4.16:

The slope of the curve = -9333

$-E_a/R$ = -9333

E_a = 77.6 kJ mol^{-1}

APPENDIX E

ADSORPTION-DESORPTION DATA

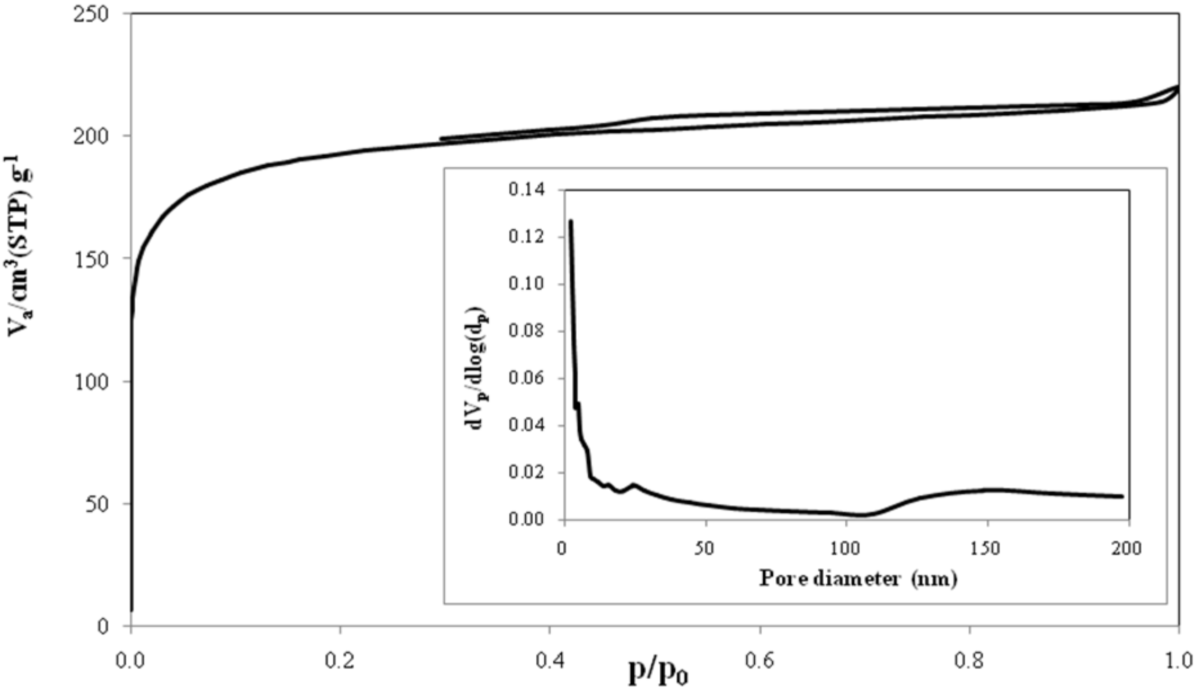

Figure E.1 N_2 adsorption/desorption isotherms and the pore size distribution of the support (charcoal activated powder) after being calcined with air zero

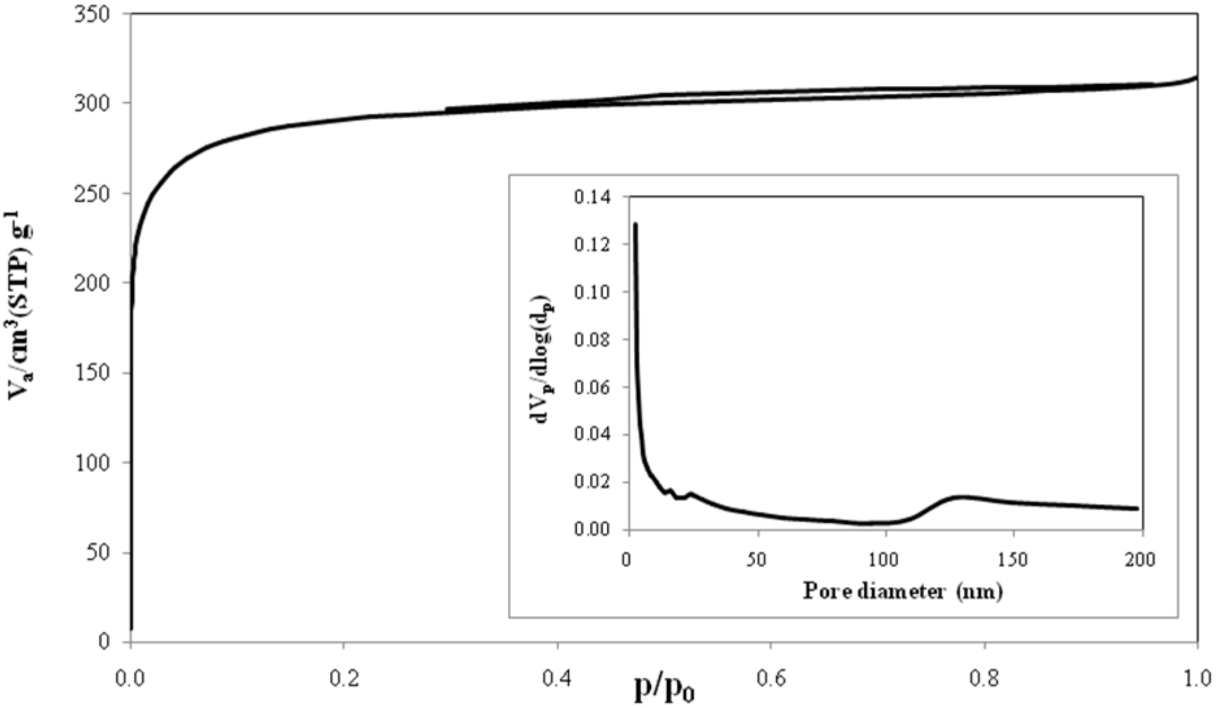

Figure E.2 N_2 adsorption/desorption isotherms and the pore size distribution of the support (charcoal activated powder) after being calcined with argon

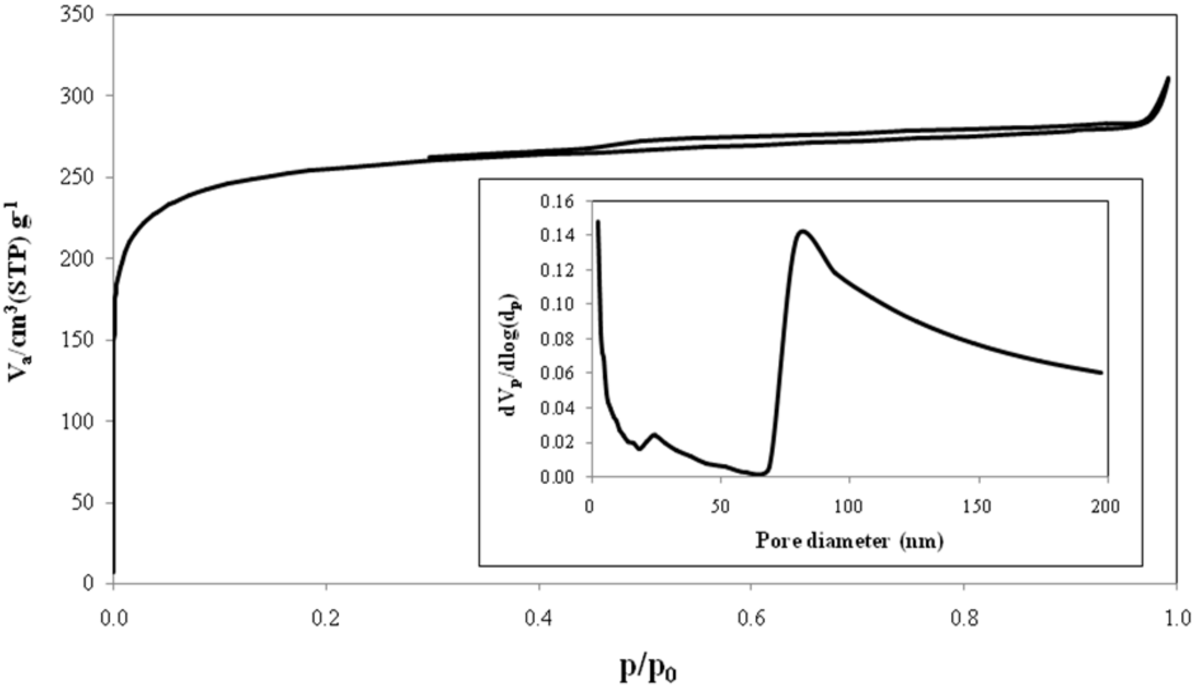

Figure E.3 N_2 adsorption/desorption isotherms and the pore size distribution of the 5%Ru/C after being calcined with air zero

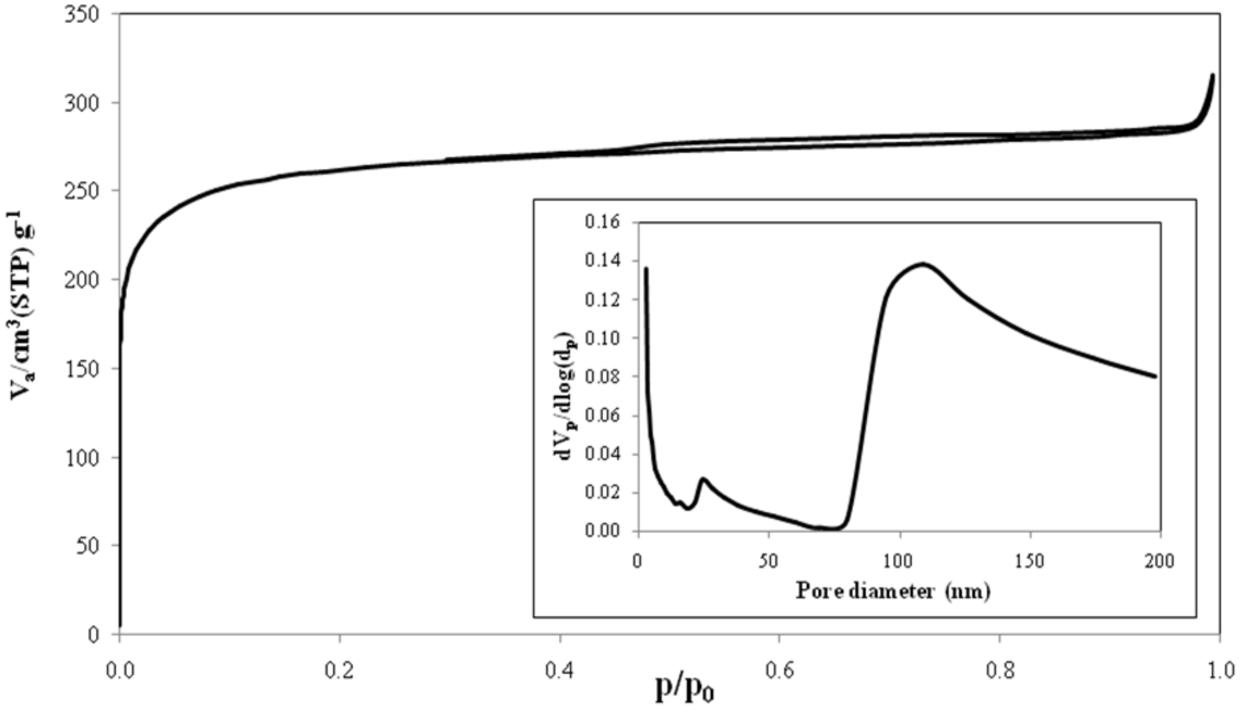

Figure E.4 N_2 adsorption/desorption isotherms and the pore size distribution of the 5%Ru/C after being calcined with argon

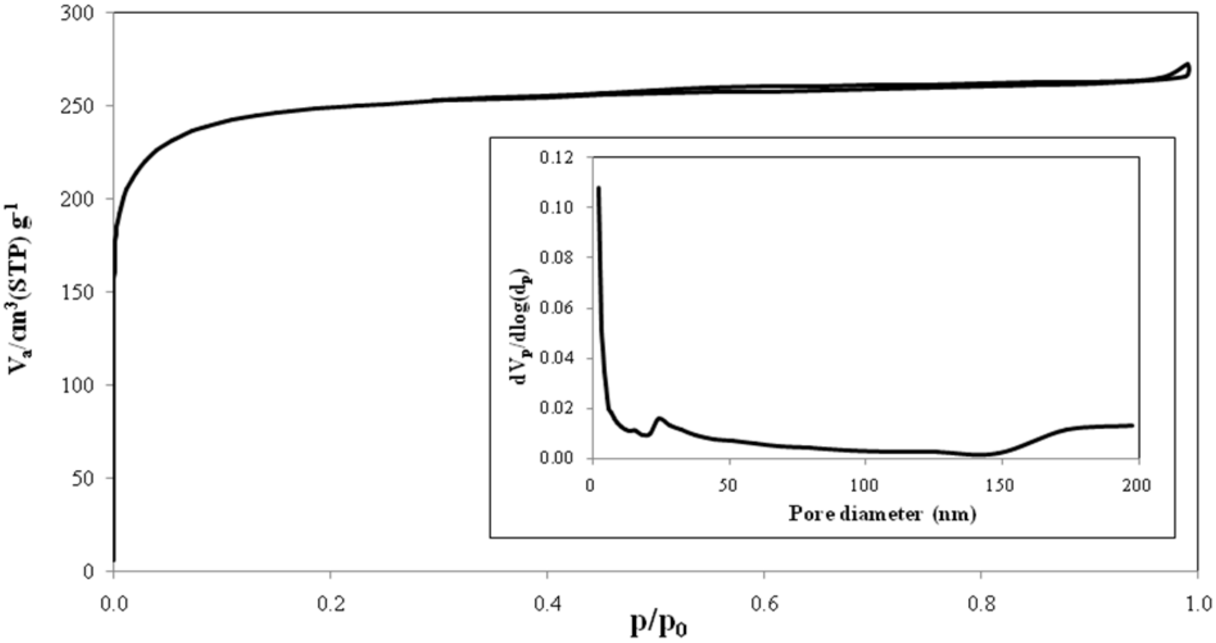

Figure E.5 N_2 adsorption/desorption isotherms and the pore size distribution of the 10%Ru/C before being calcined

APPENDIX F

RESULTS OF ISOMALTULOSE HYDROGENATION

Table F.1 Result of isomaltulose hydrogenation

Batch	**Catalyst**	**Type of support**	**Calcinations procedure**	**weight loss of catalyst after calcined**	**Volume of isomaltulose solution (ml)**	**Volume of H2 (ml)**	**Weight of catalyst (g)**	**Ratio of weight catalyst (g ml^{-1})**	**Temperature (C)**	**Pressure (bar)**	**Reaction time (h)**	**Reused catalyst**	**Conversion (%)**	**Yield (%)**	**Selectivity (%)**
1	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar(350 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	2.7	0	0
2	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar(400 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	3.1	0	0
3	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar(500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	1.2	0	0
4	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar(550 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	1.2	0	0
5	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar(700 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	3.8	0	0

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	**Catalyst**	**Type of support**	**Calcinations procedure**	**weight loss of catalyst after calcined**	**Volume of isomaltulose solution (ml)**	**Volume of H2 (ml)**	**Weight of catalyst (g)**	**Ratio of weight catalyst (g ml^{-1})**	**Temperature (C)**	**Pressure (bar)**	**Reaction time (h)**	**Reused catalyst**	**Conversion (%)**	**Yield (%)**	**Selectivity (%)**
6	5% Ru/C	Activated carbon (Sigma-Aldrich)	Air (500 °C)	1.3	139.79	78.48	0.5	3.58	120	50	5	no	3.4	0	0
7	5% Ru/C	Activated carbon (Sigma-Aldrich)	Ar:Air (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	0.0	0	0
8	10%Ru /C	Activated carbon (Sigma-Aldrich)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	26.1	23.4	100
9	5%Ru/ C	Charcoal activated powder (Panreac)	Air (500 °C)	1.4	139.79	78.48	0.5	3.58	120	50	5	no	23.5	15.5	100
10	5%Ru/ C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	26.3	22.6	100
11	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	54.8	58.2	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst $(g\ ml^{-1})$	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
12	5%Ru/ C	Charcoal activated powder (Panreac)	Air (500 °C)	1.4	139.79	78.48	0.5	3.58	120	50	1	no	0.1	6.539	100
											3	no	13.3	14.95	100
											5	no	28.5	22.63	100
											8	no	48.0	36.62	100
											10	no	59.5	45.56	100
13	5%Ru/ C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	1	no	7.8	13.51	100
											3	no	23.7	28.93	100
											5	no	41.6	42.82	100
											8	no	63.9	60.72	100
											10	no	85.3	79.94	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
14	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	1	no	20.1	27.14	100
											2	no	43.1	45.33	100
											3	no	59.4	59.41	100
											4	no	73.1	72.67	100
											5	no	85.0	84.84	100
											8	no	100.0	95.56	100
15	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	5	no	54.8	58.15	100
											6	no	72.1	77.68	100
											7	no	90.2	96.99	100
16	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500 °C)	0.1	139.79	78.48	0.5	3.58	120	50	8	no	64.4	73.4	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
17	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	139.79	78.48	0.5	3.58	120	40	1	no	0.0	21.41	100
											3	no	24.9	39.25	100
											5	no	48.5	60.41	100
											6	no	60.7	67.54	100
											8	no	77.9	81.11	100
18	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	69.89	148.38	0.25	3.58	120	40	1	no	2.5	21.95	100
											3	no	25.4	45.78	100
											5	no	58.7	69.54	100
											6	no	69.8	79.14	100
											8	no	87.8	97.08	100
19	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	139.79	78.48	0.5	3.58	120	50	1	1	29.2	24.67	100
											5	1	90.8	85.48	100
											6	1	100	90	100
											7	1	100	96.44	100
											8	1	100	93.6	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
20	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	139.79	78.48	0.5	3.58	120	50	1	2	15.8	18.15	100
											5	2	76.2	74.98	100
											6	2	90.7	86.24	100
											7	2	95.7	92.94	100
											8	2	100	93.91	100
21	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	139.79	78.48	0.5	3.58	120	50	1	3	9.0	14.43	100
											3	3	30.2	29.93	100
											5	3	51.7	54.98	100
											6	3	67.1	68.57	100
23	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	83.87	134.40	0.5	5.96	120	50	1	no	15.0	42.71	100
											2	no	56.0	72.39	100
											3	no	82.6	86.48	100
											4	no	93.2	98.35	100
											5	no	100	101.3	100
											6	no	100	99.35	100
											7	no	100	97.42	100
											8	no	100	92.88	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
24	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	83.87	134.4	0.5	5.96	100	50	1	no	23.2	23.2	100
											2	no	37.7	37.7	100
											3	no	45.9	45.9	100
											4	no	56.2	56.2	100
											5	no	67.0	67.0	100
											6	no	77.9	77.9	100
											7	no	83.3	83.3	100
											8	no	86.1	86.1	100
25	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	83.87	134.4	0.5	5.96	120	40	1	no	30.0	30.0	100
											2	no	60.4	60.4	100
											3	no	78.9	78.9	100
											4	no	92.0	92.0	100
											5	no	100.0	100.0	100
											6	no	100.0	100.0	100
											7	no	100.0	100.0	100
											8	no	100.0	100.0	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
26	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	83.87	134.4	0.5	5.96	120	60	1	no	22.3	22.3	100
											2		49.4	49.4	100
											3		73.8	73.8	100
											4		88.9	88.9	100
											5		94.7	94.7	100
											6				
27	10%Ru /C	Charcoal activated powder (Panreac)	Ar (500°C)	0.1	83.87	134.4	0.8	5.96	120	50	1	no	15.6	15.6	100
											2		39.7	39.7	100
											3		60.6	60.6	100
											4		75.3	75.3	100
											5		91.8	91.8	100
											6		100.0	100.0	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	Catalyst	Type of support	Calcinations procedure	weight loss of catalyst after calcined	Volume of isomaltulose solution (ml)	Volume of H2 (ml)	Weight of catalyst (g)	Ratio of weight catalyst (g ml^{-1})	Temperature (C)	Pressure (bar)	Reaction time (h)	Reused catalyst	Conversion (%)	Yield (%)	Selectivity (%)
28	10%Ru /C*	Charcoal activated powder (Panreac)	Ar=500 C	0.1	83.87	134.4	1.2	5.96	120	50	1	no	35.9	35.9	100
											2		75.9	75.9	100
											3		100.0	100.0	100
											4		100.0	100.0	100
											5		100.0	100.0	100
											6		100.0	100.0	100
29	10%Ru /C*	Charcoal activated powder (Panreac)	Ar=500 C	0.1	83.87	134.4	0.5	5.96	120	30	1	no	27.61	25.9	100
											2		48.95	45.7	100
											3		62.72	55.8	100
											4		77.36	72.9	100
											5		89.81	84.3	100
											6		98.06	99.1	100
											7		100	100	100
											8		100	100	100

Table F.1 Result of isomaltulose hydrogenation (continuous)

Batch	**Catalyst**	**Type of support**	**Calcinations procedure**	**weight loss of catalyst after calcined**	**Volume of isomaltulose solution (ml)**	**Volume of H2 (ml)**	**Weight of catalyst (g)**	**Ratio of weight catalyst (g ml^{-1})**	**Temperature (C)**	**Pressure (bar)**	**Reaction time (h)**	**Reused catalyst**	**Conversion (%)**	**Yield (%)**	**Selectivity (%)**
30	10%Ru /C*	Charcoal activated powder (Panreac)	Ar=500 C	0.1	83.87	134.4	1.2	5.96	130	50	1	no	36.0	44.5	100
											2		69.2	75.0	100
											3		88.4	97.4	100
											4		91.2	100.0	100
											5		94.1	100.0	100
											6		99.3	100.0	100

APPENDIX G

Langmuir-Hinshelwood-Hougen-Watson (LHHW) KINETIC

Non-competitive equation:

Assume: Mass transfer limit

Step1: Isomaltulose $+ \theta \xrightarrow{K_{Isomaltulose}} \theta_{Isomaltulose}$

Step2: $H_2 + \theta \xrightarrow{K_{H2}} \theta_{H2}$

Step3: $\theta_{Isomaltulose} + \theta_{H2} \xrightarrow{K} \theta_{Isomalt} + \theta$

Step3: $\theta_{Isomalt} \xrightarrow{K_{Isomalt}}$ Isomalt

Rate of reaction: $-r_{isomaltulose} = k\theta_{isomaltulose}\theta_{H_2}$ (G.1)

At Isomaltulose

Rate of adsorption $= k(1-\theta_{isomaltulose})C_{isomaltulose}$ (G.2)

Rate of desorption $= k'(\theta_{isomaltulose})$ (G.3)

At equilibrium: G.2=G.3 so

$$k(1-\theta_{isomaltulose})C_{isomaltulose} = k'(\theta_{isomaltulose}) \quad \text{(G.4)}$$

When $K_{isomaltulose} = k/k'$ (adsorption constants of isomaltulose)

So from G.4 is $K_{isomaltulose}(1-\theta_{isomaltulose})C_{isomaltulose} = \theta_{isomaltulose}$

$$K_{isomaltulose}C_{isomaltulose} = \theta_{isomaltulose} + C_{isomaltulose}K_{isomaltulose}\theta_{isomaltulose}$$

$$K_{isomaltulose}C_{isomaltulose} = \theta_{isomaltulose}(1 + C_{isomaltulose}K_{isomaltulose})$$

$$\theta_{isomaltulose} = \frac{C_{isomaltulose}K_{isomaltulose}}{1 + C_{isomaltulose}K_{isomaltulose}} \quad \text{(G.5)}$$

At hydrogen

Rate of adsorption $= k(1-\theta_{H_2})P_{H_2}$ (G.6)

Rate of desorption $= k'(\theta_{H_3})$ (G.7)

At equilibrium: G.6=G.7 so

$$k(1-\theta_{H_2})P_{H_2} = k'(\theta_{H_3}) \qquad \text{(G.8)}$$

When $K_{H_2} = {}^{k}\!/_{k'}$ (adsorption constants of hydrogen)

So from G.4 is $K_{H_2}(1-\theta_{H_2})P_{H_2} = \theta_{H_2}$

$$K_{H_2}P_{H_2} = \theta_{H_2} + P_{H_2}K_{H_2}\theta_{H_2}$$

$$K_{H_2}P_{H_2} = \theta_{H_2}(1+P_{H_2}K_{H_2})$$

$$\theta_{H_2} = \frac{P_{H_2}K_{H_2}}{1+P_{H_2}K_{H_2}} \qquad \text{(G.9)}$$

So from (G.1)

$$-r_{\text{isomaltulose}} = \frac{kC^n_{\text{isomaltulose}}P^m_{\text{H}_2}K_{\text{H}_2}K_{isomaltolose}}{(1+K_{\text{H}_2}P^m_{\text{H}_2})(1+K_{\text{isomaltulose}}C^n_{\text{isomaltulose}})} \qquad \text{(G.10)}$$

APPENDIX H

RESULTS OF RATE REACTION

Table H.1 Result of rate of reaction

Effect of gas in calcination catalyst

Air

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.41	-2.38E-05
10800	1.28	-2.33E-05
18000	1.15	-2.28E-05
28800	0.91	-2.20E-05
36000	0.75	-2.16E-05

Argon

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.29	-2.59E-05
10800	1.10	-2.56E-05
18000	0.91	-2.53E-05
28800	0.63	-2.49E-05
36000	0.29	-2.46E-05

Effect of catalyst metal loading

5%Ru/C catalyst

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.29	-2.59E-05
10800	1.10	-2.56E-05
18000	0.91	-2.53E-05
28800	0.63	-2.49E-05
36000	0.29	-2.46E-05

10%Ru/C

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.14	-7.89E-05
10800	0.66	-5.88E-05
18000	0.26	-3.86E-05
28800	0.00	-8.36E-06

Effect of amount of catalyst

Catalyst 0.5 g

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.10	-1.42E-04
7200	0.69	-1.10E-04
10800	0.32	-7.67E-05
14400	0.13	-4.40E-05
18000	0.00	-1.12E-05
21600	0.00	2.15E-05
25200	0.00	5.43E-05
28800	0.00	8.71E-05

Catalyst 1.2 g

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.00	-1.69E-04
7200	0.44	-1.38E-04
10800	0.00	-1.07E-04
14400	0.00	-7.62E-05
18000	0.00	-4.52E-05
21600	0.00	-1.42E-05

Effect of H_2 on hydrogenation

Volume of hydrogen: 78 ml

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.26	-5.64E-05
10800	1.04	-4.92E-05
18000	0.78	-4.20E-05
21600	0.64	-3.84E-05
28800	0.38	-3.12E-05

Volume of hydrogen: 148 ml

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.43	-6.71E-05
10800	1.12	-6.14E-05
18000	0.74	-5.56E-05
21600	0.50	-5.27E-05
28800	0.19	-4.70E-05

Effect of reaction temperature on hydrogenation

Condition	Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
30 bar, 120 ^{o}C	3600	1.18	-1.88E-03
	7200	0.84	-1.56E-03
	10800	0.66	-1.25E-03
	14400	0.43	-9.26E-04
	18000	0.21	-6.06E-04
	21600	0.04	-2.87E-04
	25200	0.00	3.30E-05
	28800	0.00	3.52E-04

Condition	Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
40 bar, 120 C	3600	1.08	-2.23E-03
	7200	0.71	-1.82E-03
	10800	0.41	-1.41E-03
	14400	0.17	-1.00E-03
	18000	0.00	-5.94E-04

Condition	Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
50 bar, 120 C	3600	1.10	-2.85E-03
	7200	0.63	-2.19E-03
	10800	0.29	-1.53E-03
	14400	0.11	-8.80E-04
	18000	0.00	-2.25E-04

Condition	Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
50 bar, 100 C	3600	1.21	-8.27E-04
	7200	1.03	-7.94E-04
	10800	0.94	-7.61E-04
	14400	0.82	-7.28E-04
	18000	0.66	-6.94E-04
	21600	0.48	-6.61E-04
	25200	0.37	-6.28E-04
	28800	0.32	-5.95E-04

Condition	Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
50 bar, 130 C	3600	0.78	-2.95E-03
	7200	0.36	-1.94E-03
	10800	0.04	-9.36E-04
	14400	0.00	7.18E-05
	18000	0.00	1.08E-03

Stability of 10%Ru/C catalyst for hydrogenation of isomaltulose

Fresh

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.14	-9.14E-05
18000	0.76	-7.70E-05
21600	0.49	-6.14E-05
25200	0.18	-1.06E-04
28800	0.00	-1.20E-04

First time

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.01	-6.83E-05
18000	0.16	-4.96E-05
21600	0.00	-4.49E-05
25200	0.00	-4.02E-05
28800	0.00	-3.56E-05

Second time

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.22	-7.13E-05
18000	0.42	-4.51E-05
21600	0.17	-3.86E-05
25200	0.08	-3.20E-05
28800	0.00	-2.55E-05

Third time

Time (s)	Concentration of isomaltulose (mol l^{-1})	Rate of reaction (mol l^{-1} s^{-1})
3600	1.28	-3.89E-05
18000	0.78	-3.83E-05
21600	0.58	-3.81E-05
28800	0.36	-3.79E-05

VITA

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PUBLICATION

Suratsawadee Sukeesan, Worapon Kiatkittipong and Prasert Pavasant. PRODUCTION OF SPECIAL SUGAR WITH HYDROGENATION METHOD. Pure and Applied Chemistry International Conference, Chiang Mai University, January 11-13, 2012.