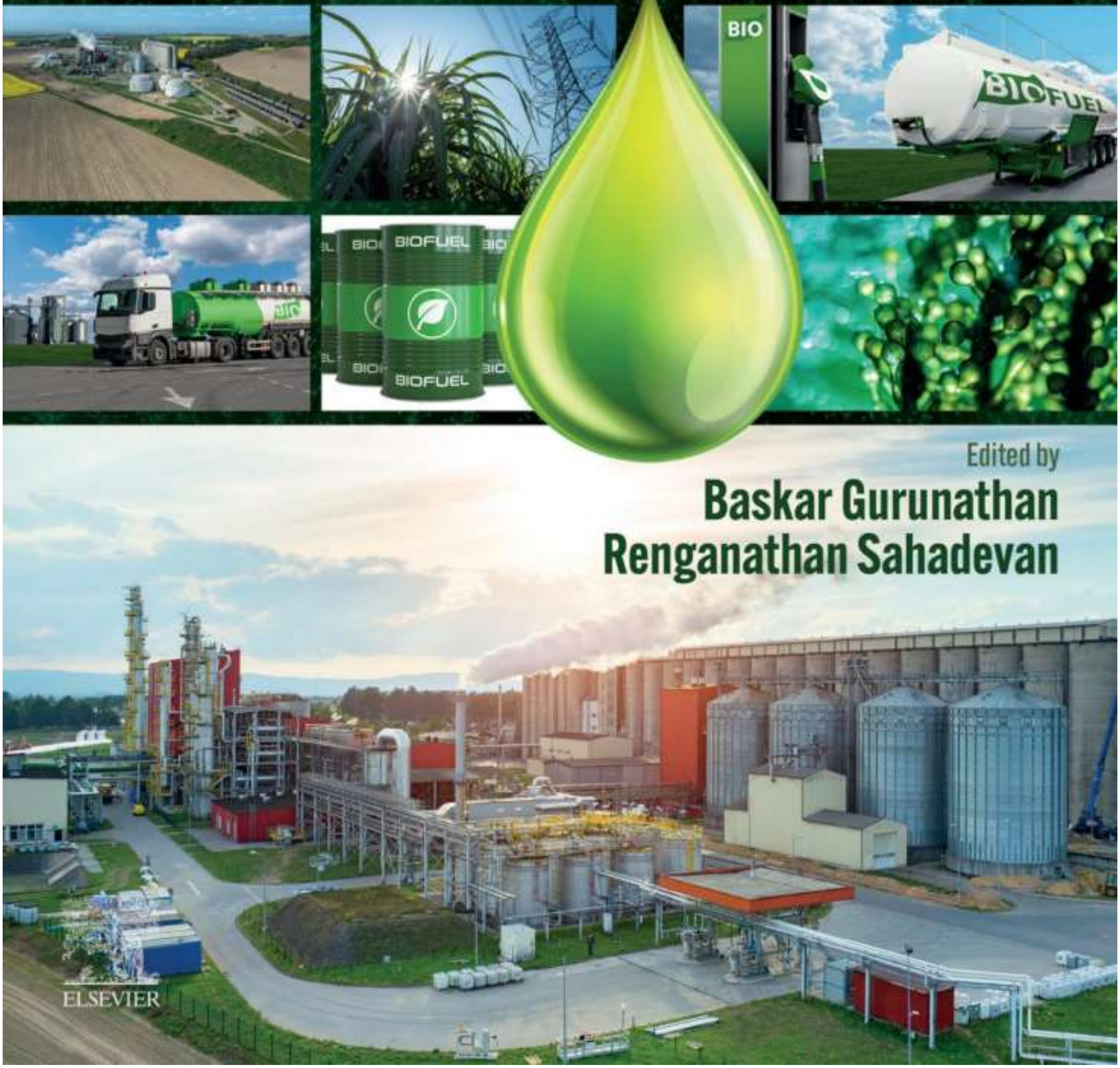
BIOFUELS AND BIOENERGY

A Techno-Economic Approach



Edited by

Baskar Gurunathan
Renganathan Sahadevan

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A Techno-Economic Approach

Edited by

BASKAR GURUNATHAN
Department of Biotechnology, St. Joseph's College of Engineering,
Chennai, Tamil Nadu, India

RENGANATHAN SAHADEVAN
Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

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Contents

Section I Biorefinery approaches in biofuels and bioenergy production

4. Evaluation of activated sludge derived from wastewater treatment process as a potential biorefinery platform 71

Jyotika Thakur and Shyam Kumar Masakapalli

5. Insights into the impact of biorefineries and sustainable green technologies on circular bioeconomy 85

R. Kheerthivasan, Nadeem Siddiqui, E. Nakkeeran and K. Divakar

Section II Biofuels and bioenergy production - I

11. Production of cellulosic butanol by clostridial fermentation: a superior alternative renewable liquid fuel 263

Gobinath Rajagopalan and Chandraraj Krishnan

12. Biobutanol separation using ionic liquids as a green solvent 291

Kailas L. Wasewar

13. Synergistic prospects of microalgae after wastewater treatment to be used for biofuel production 323

Louis Anto Nirmal, Sholinghur Asuri Bhakthochidan, Ravichandran Vishal, Veeraraghavan Babulu Roshini and Samuel Jacob

Section III Biofuels and bioenergy production—II

Section IV Technoeconomic and environmental impact analysis of biofuels and bioenergy

25. Techno-economic analysis of biodiesel production from nonedible biooil using catalytic transesterification 601

Naveenkumar Rajendran, Ashok Pandey, Edgard Gnansounou, Baskar Gurunathan and Jeehoon Han

26. Technoeconomic analysis of biofuel production from marine algae 627

G. Kalavathy, Ashok Pandey, Edgard Gnansounou and Baskar Gurunathan

31. Environmental impact analysis of biofuels and bioenergy: a globalperspective 739

J. Iyyappan, Baskar Gurunathan, M. Gopinath, A. Vaishnavi, S. Prathiba, V. Kanishka, K. Gomathi and V. Dhithya

32. Environmental impacts of biofuels and their blends: a case study on waste vegetable oil-derived biofuel blends 755

Pritam Dey and Srimanta Ray

33. Solid biofuel production, environmental impact, and technoeconomic analysis 771

Elsa Cherian, Lakshmi Mohan and K.A. Anju

List of contributors

Nidhi Agnihotri
Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, Uttar Pradesh, India

R. Anantharaj
Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, Tamil Nadu, India

K.A. Anju
Department of Food Technology, SAINTGITS College of Engineering, Kottayam, Kerala, India

Umaiyambika Neduvel Annal
Biofuels Lab, Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

Kirtikumar C. Badgujar
Department of Chemistry, Institute of Chemical Technology, Mumbai, Maharashtra, India; Department of Chemistry, SIES College of Arts, Science & Commerce, Mumbai, Maharashtra, India

Vivek C. Badgujar
Department of Chemistry, Pratap College of Arts, Science & Commerce, Amalner, Maharashtra, India

Sholinghur Asuri Bhakthochidan
Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Bhalchandra M. Bhanage
Department of Chemistry, Institute of Chemical Technology, Mumbai, Maharashtra, India

Maria Susai Boobalan
Department of Chemistry, College of Natural and Computational Sciences, Haramaya University, Dire Dawa, Oromiya Regional State, Ethiopia

Elsa Cherian
Department of Food Technology, SAINTGITS College of Engineering, Kottayam, Kerala, India

S. Chozhavendhan
Department of Biotechnology, VSB Engineering College, Karur, Tamil Nadu, India

Pinaki Dey
Department of Biotechnology, Karunya Institute of Technology and Sciences, Coimbatore, Tamil Nadu, India

Pritam Dey
Department of Chemical Engineering, National Institute of Technology Agartala, Jirania, Tripura, India

Bijay Dhakal
Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada

V. Dhithya
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

Kevin Joseph Dilip
Department of Life Sciences, National Dong Hwa University, Taipei, Taiwan, China

K. Divakar
Department of Biotechnology, Sri Venkateswara College of Engineering, Sriperumbudur, Tamil Nadu, India

Kaleab Bizuneh Gebeyehu
Chemical Engineering, Haramaya Institute of Technology, Haramaya University, Dire Dawa, Oromiya Regional State, Ethiopia

Jenet George
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Manjot Gill
Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada

D. Gnana Prakash
Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, Tamil Nadu, India

Edgard Gnansounou
Bioenergy and Energy Planning Research Group, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

K. Gomathi
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

B. Gopalakrishnan
Department of Chemical Engineering, Annamalai University, Chidambaram, Tamil Nadu, India

M. Gopinath
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

Bhargavi Gunturu
Bionanomaterials laboratory, Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

Geetika Gupta
Department of Biotechnology, Thapar Institute of Engineering and Technology, Patiala, Punjab, India

Baskar Gurunathan
Department of Biotechnology, St. Joseph's College of Engineering, Chennai, Tamil Nadu, India

Adam Shahul Hameed
Biofuels laboratory, Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

Jeehoon Han
School of Semiconductor and Chemical Engineering, Jeonbuk National University, Jeonju, Republic of Korea

J. Iyyappan
Department of Biotechnology, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS), Chennai, Tamil Nadu, India

Samuel Jacob
Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Mani Jayakumar
Chemical Engineering, Haramaya Institute of Technology, Haramaya University, Dire Dawa, Oromiya Regional State, Ethiopia

G. Kalavathy
Department of Biotechnology, St. Joseph's College of Engineering, Chennai, Tamil Nadu, India

V. Kanishka
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

Natchimuthu Karmegam
Department of Botany, Government Arts College (Autonomous), Salem, Tamil Nadu, India

S. Karthikadevi
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

Ilango Karuppasamy
Department of Electrical and Electronics Engineering, Amrita Vishwa Vidyapeetham, Coimbatore, Tamil Nadu, India

A. Kaviprabha
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

R. Kheerthivasan
Department of Biotechnology, Sri Venkateswara College of Engineering, Sriperumbudur, Tamil Nadu, India

Chandraraj Krishnan
Department of Biotechnology, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India

Amit Kumar
Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada

Selvakumar Kuppusamy Vaithilingam
School of Chemical and Bio Engineering, Dire Dawa University Institute of Technology, Dire Dawa University, Dire Dawa, Ethiopia

Vinoj Kurian
Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada

Ratna Dewi Kusumaningtyas
Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Kampus UNNES, Semarang, Indonesia

Ririn Mahmudati
Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Kampus UNNES, Semarang, Indonesia

Prasad Mandade
Bioenergy and Energy Planning Research Group, EPFL, Lausanne, Switzerland

Vijay Mani
Department of Chemical Engineering, Annamalai University, Chidambaram, Tamil Nadu, India

Shyam Kumar Masakapalli
BioX Center, School of Basic Sciences, Indian Institute of Technology Mandi, Kamand, Himachal Pradesh, India

Samir Meramo
Sustainable Innovation Office, Novo Nordisk Foundation Center for Biosustainability, Technical University of Denmark, Lyngby, Denmark

Bishwambhar Mishra
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Lakshmi Mohan
Department of Food Technology, SAINTGITS College of Engineering, Kottayam, Kerala, India

Upasana Mohanty
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Monoj Kumar Mondal
Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, Uttar Pradesh, India

A. Muthu Kumara Pandian
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

Praveena Nagarajan
Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

E. Nakkeeran
Department of Biotechnology, Sri Venkateswara College of Engineering, Sriperumbudur, Tamil Nadu, India

Arunodhaya Natarajan
Department of Petroleum Engineering, Rajiv Gandhi College of Engineering, Chennai, Tamil Nadu, India

Jayato Nayak
Department of Chemical Engineering, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil, Tamil Nadu, India

Yogesh M. Nimdeo
Department of Chemical Engineering, Indian Institute of Technology Jammu, Jammu, India

Louis Anto Nirmal
Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Ashok Pandey
CSIR-Indian Institute of Toxicology Research, Lucknow, Uttar Pradesh, India

Sivakumar Pandian
School of Petroleum Technology, Pandit Deedayal Energy University, Gandhinagar, Gujarat, India

Senthil Kumar Ponnusamy
Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, Tamil Nadu, India

Haniif Prasetiawan
Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Kampus UNNES, Semarang, Indonesia

S. Prathiba
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

A. Priyanka
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Indah Purnamasari
Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Kampus UNNES, Semarang, Indonesia

G.B. Radhika
Department of Chemical Engineering, B V Raju Institute of Technology, Narsapur, Medak Dist, Telangana, India

Gobinath Rajagopalan
Industrial Biotechnology Laboratory, Faculty of Life Sciences and Biotechnology, South Asian University (SAU), New Delhi, India

M. Rajamehala
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

Y. Rajasri
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Naveenkumar Rajendran
Department of Biotechnology, St. Joseph's College of Engineering, Chennai, Tamil Nadu, India; School of Chemical Engineering, Jeonbuk National University, Jeonju, Republic of Korea

Geethalakshmi Ramakrishnan
Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

P. Ramesh
Department of Chemical Engineering, B V Raju Institute of Technology, Narsapur, Medak Dist, Telangana, India

Panneerselvam Ranganathan
Department of Chemical Engineering, National Institute of Technology Calicut, Kozhikode, Kerala, India

Abiram Karanam Rathankumar
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Srimanta Ray
Department of Chemical Engineering, National Institute of Technology Agartala, Jirania, Tripura, India

C. Nagendranatha Reddy
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Veeraraghavan Babulu Roshini
Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Renganathan Sahadevan
Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

Kongkona Saikia
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

P. Saranya
Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, Tamil Nadu, India

Priyanka Saravanan
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Anna Shaji
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

A. Shalini
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Nadeem Siddiqui
Department of Biotechnology, Koneru Lakshmaiah Education Foundation, Guntur, Andhra Pradesh, India

G. Srinivas
Department of Chemical Engineering, B V Raju Institute of Technology, Narsapur, Medak Dist, Telangana, India

T. Srinivas
Department of Chemical Engineering, B V Raju Institute of Technology, Narsapur, Medak Dist, Telangana, India

Renugaa Su
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

V. Swapna
Department of Chemical Engineering, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Jyotika Thakur
BioX Center, School of Basic Sciences, Indian Institute of Technology Mandi, Kamand, Himachal Pradesh, India

Vinoth Kumar Vaidyanathan
Integrated Bioprocessing Laboratory, Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

A. Vaishnavi
Department of Biotechnology, Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Chennai, Tamil Nadu, India

M. Vichitra
Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai, Tamil Nadu, India

M. Vijay Pradhap Singh
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Tamil Nadu, India

Y. Vineetha
Department of Biotechnology, Chaitanya Bharathi Institute of Technology, Hyderabad, Telangana, India

Ravichandran Vishal
Department of Biotechnology, School of Bioengineering, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Kailas L. Wasewar
Advance Separation and Analytical Laboratory (ASAL), Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT), Nagpur, Maharashtra, India

E. Yuvanashree
Biofuels Lab, Centre for Biotechnology, Anna University, Chennai, Tamil Nadu, India

Preface

Biorefineries utilize renewable sources for the production of various biofuels using integrated approaches. Currently, biorefinery approaches are facing many technical challenges. It is important to refine biorefinery concepts to overcome these challenges and make commercially viable biorefineries. This book *Biofuels and Bioenergy: A Techno-Economic Approach* covers the latest developments in biorefinery approaches for the production of various biofuels and bioenergy by the utilization of various solid and liquid renewable feedstocks. This book also covers biorefinery approaches for circular bioeconomy, techno-economic analysis of biofuels production, environmental impact analysis of biofuels, microbial electrosynthesis of biofuels, and performance of biodiesel in a diesel engine. This book provides comprehensive information on biorefinery approaches for biofuels and bioenergy under four sections comprising 33 chapters as detailed here.

Section I focused on biorefinery approaches in biofuels and bioenergy production. This section covers various chapters such as boundaries and openings of biorefineries toward sustainable biofuel production, a perspective on the biorefinery approaches for bioenergy production in a circular bioeconomy process, a comprehensive integration of biorefinery concepts for the production of biofuels from lignocellulosic biomass, evaluation of activated sludge derived from wastewater treatment process as a potential biorefinery platform, and insights into the impact of biorefineries and sustainable green technologies on circular bioeconomy.

Section II comprising nine chapters focused on fermentation technology for ethanol production: current trends and challenges, improved enzymatic hydrolysis of lignocellulosic waste biomass: most essential stage to develop cost-effective bio-fuel production, advances and sustainable conversion of waste lignocellulosic biomass into biofuels, lignocellulosic biomass as an alternate source for next-generation biofuel, process intensification of biobutanol production, production of n-butanol by clostridial fermentation: a superior alternative renewable liquid fuel, biobutanol separation using ionic liquids as a green solvent, synergistic prospects of microalgae in wastewater treatment and third-generation biofuel production and concurrent reduction of carbon dioxide and generation of biofuels by electrified microbial systems—concepts and perspectives.

Section III comprising eight chapters focused on biofuels and bioenergy production such as challenges and opportunities in large-scale production of biodiesel, lipid-derived biofuel: production methodologies, interesterification reaction of vegetable oil and alkyl acetate as alternative route for glycerol-free biodiesel synthesis, recent advances of lipase catalyzed greener production of biodiesel in organic reaction media: economic and sustainable viewpoint, efficient utilization of biomass-derived heterogeneous catalyst for biodiesel production, catalytic pyrolysis for upgrading of bio-oil obtained from biomass, recent trends in pyrolysis and gasification of lignocellulosic biomass and experimental investigation of performance of biodiesel with different blends in a diesel engine.

Section IV is mainly about the techno-economic and environmental impact analysis of biofuels and bioenergy. This section includes the chapters such as techno-economic evaluation of 2G ethanol production with co-products from rice straw, techno-economic analysis for production of biodiesel using noncatalytic transesterfication, techno-economic analysis of biodiesel production from nonedible biooil using catalytic transesterfication, techno-economic analysis of biofuels production from marine algae, techno-economic assessment of biofuel production using thermochemical pathways, modeling and techno-economic analysis of biogas production from waste food, biofuels production from algal biomass: environmental impact and techno-economic analysis, computer-aided environmental and techno-economic analyses as tools for development of biorefineries under the circular bioeconomy approach, environmental impact analysis of biofuels and bioenergy-a global perspective, environmental impacts of biofuels and their blends: a case study on waste vegetable oil—derived biofuel blends and solid biofuels production, environmental impact and techno-economic analysis.

Biofuels and Bioenergy: A Techno-Economic Approach is a hands-on reference for faculty members, researchers, scientists, and practicing engineers working on various fields of bioenergy, biorefinery, and biofuels' production. This book is a good source of information addressing industrial problems relevant to undergraduate, postgraduate, and research students under different academic departments such as biotechnology, chemical, energy, and environmental engineering in various universities and academic institutions.

Baskar Gurunathan
Renganathan Sahadevan

CHAPTER 17

Interesterification reaction of vegetable oil and alkyl acetate as alternative route for glycerol-free biodiesel synthesis

Ratna Dewi Kusumaningtyas, Indah Purnamasari, Ririn Mahmudati and Haniif Prasetiawan
Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Kampus UNNES, Semarang, Indonesia

17.1 Introduction

The world population growth and industrial development has led to the increasing of the global energy needs. To date, fossil energy, which includes petroleum, coal, and natural gas, has fulfilled around 80% of the world energy demand. In particular, petroleum shares approximately 90% of the fuel consumption in the transportation sector. Fossil energy dominates the total energy supply (TES) source as reported by the International Energy Agency (IEA) (IEA, 2020). Utilization of fossil fuel as major energy resources has embarked on several dares related to the oil reserves decimation and environmental issues. The data provided by the U.S. Energy Information Administration indicates that the petroleum and other liquid fuel consumption throughout 2019−22 tends to be higher than its production (EIA, 2020a). This unbalanced condition is predicted to be severer in the future due to the growth of population, transportation, and industrial sectors. In fact, the worse condition happens in some countries with significant declining in oil reserves.

At the same time, fossil fuel is under pressure to respond to the climate change issue. Concerning the environmental aspects, combustion of fossil fuel is stated as the major contributor of the greenhouse gases' (such as CO_2, NO_x) emission to the atmosphere, causing the increasing temperature of the planet and an extreme climate change during the last few years. Therefore the energy transition from fossil-based fuel to carbon-neutral or zero carbon energy resources is important for carbon reduction in energy sector. This is also in line with the policy of the United Nation which has set up the Sustainable Development Goal (SDG) 7 in terms of affordable and clean energy by 2030 (Asadikia et al., 2021). According to the Paris Climate Agreement 2015, it is

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also expected to confine the global temperature increase to 1.5°C, to lessen the negative effect of climate change, and to achieve net-zero emission of energy utilization by 2050 (Kato and Kurosawa, 2019; Lopez et al., 2021). Furthermore, the new paradigm of the energy sustainability established by the World Energy Council comprises the three main attributes, which is called Trilemma: energy security, energy equity, and environmental sustainability of energy system (World Energy Council, 2020). In this context, energy also has enduring mission to reach a better lives for people (Gadonneix et al., 2020).

Based on the SDG 7 and Trilemma concept, enhancement in energy security and sustainability should proceed concurrently. One of the key to provide affordable energy with low environmental negative impact is deploying renewable energy as substitute to the fossil-based energy (Bertheau, 2020; Gielen et al., 2019). Renewable energy, especially with zero carbon or neutral carbon characteristic, has great potential to contribute in lowering the greenhouse gases' emission. Innovation in its process technology likewise could decrease the production cost. Yet, it expected that renewable energy can afford 8% of the global energy consumption. Enhancing the portion of renewable energy in the world's energy consumption is one among the three main targets of SDG 7 for 2030 (Santika et al., 2020). Therefore it is essential to work on the renewable energy development, particularly which is applied for transportation as the biggest CO_2 emitter. Based on IEA projection for change in the global energy mix 2019−40, it is indicated that bioenergy is among the important renewable energy (CAPP, 2020).

Biodiesel is one of bioenergy. It is derived from vegetable oil which can be utilized as substitute for petroleum diesel. It is regarded as carbon neutral since the vegetable oils as common feedstock of biodiesel are obtained from plants, in which plants take up carbon dioxide (CO_2) from the air for photosynthesis. The absorption of CO_2 by these plants thus counterbalances the CO_2 released during the production and combustion of biodiesel as presented in Fig. 17.1 (EIA, 2020b). Therefore substituting fossil fuel with biodiesel is beneficial for decarbonizing the energy system.

17.2 Biodiesel

Biodiesel is classified as biomass-based diesel fuels, which can be used as substitute of petroleum diesel. Utilization of biodiesel as alternative diesel fuel is strategic since diesel engine is extensively used in many sectors, for instance agriculture, transportation, and industry (Ma et al., 2021; Ogunkunle and Ahmed, 2019). Compared to fossil diesel, biodiesel shows many advantages, namely, nontoxic, biodegradable, safer due to its higher flash point (less inflammable), and more environmentally friendly. Biodiesel also holds higher cetane number better fuel lubricity, superior ignition performance, and higher combustion efficiency. Additionally, combustion of biodiesel releases lower

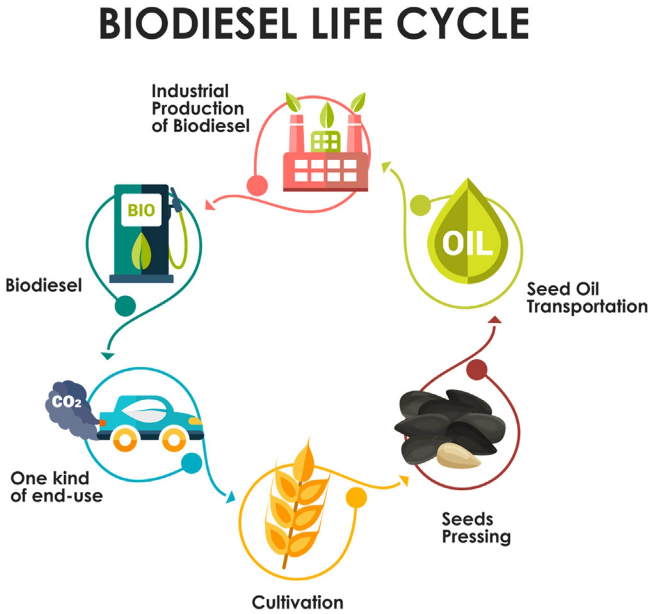

Figure 17.1 Biodiesel as carbon-neutral renewable energy source.

emission in the form of particulates, CO, SO_2, hydrocarbon, as well as other air toxics and pollutants (Kusumaningtyas et al., 2014; Ma et al., 2021; Traviss and Treadwell, 2018). And again, owing to its carbon-neutral characteristic, utilization of biodiesel as fossil diesel substitute will contribute to reduced climate change and global warming.

Biodiesel is usually applied as diesel engine fuel in form of biodiesel—petroleum diesel blending in various ratios, such as 2%, 5%, 7%, 10%, 20%, or 30%. The higher ratio or even pure biodiesel can be utilized, as well (Ogunkunle and Ahmed, 2019; Widjanarko et al., 2020). Biodiesel has been used extensively in many countries as part of the government policy on renewable energy, such as B20 in the United States under the Energy Policy Act of 1992 (AFDC, 2008), B30 in Indonesia under MEMR Regulation Number 12/2015 (Santika et al., 2020), B15 in Malaysia, and B10 in Thailand (Zulqarnain et al., 2020).

Biodiesel, which is also currently known as fatty acid methyl ester (FAME), is commonly produced using vegetable oils as raw material. In fact, vegetable-based biofuel application has long been known since Rudolf Diesel employed peanut oil as the fuel for the diesel engine and demonstrated it at the world fair in Paris in 1990 (Ma and Hanna, 1999; Ogunkunle and Ahmed, 2019). But, then, the popularity of this biofuel was decreasing because of the fossil-fuel booming in the early 20th century. When the issue on the oil reserve exhaustion and energy crisis emerged in 1980s, biodiesel was gaining attention for the second time as alternative energy to the fossil diesel fuel. However, vegetable oil cannot be directly applied for today's diesel engine due to its exceptionally high viscosity. To fulfill the specification which suits the current diesel engine, vegetable oil should be processed to reduce its viscosity. The product is nowadays named biodiesel. There are several methods to convert vegetable oils into biodiesel, among others:

1. Pyrolysis
2. Microemulsification
3. Dilution
4. Two-step preparation: hydrolysis and methyl esterification
5. Transesterification
6. Interesterification

Pyrolysis is thermal breakdown of organic materials in the absence of oxygen. It can be direct or catalytic thermal cracking. Triglyceride pyrolysis results in hydrocarbons and oxygenated organic compounds, such as alkanes, alkenes, alkadienes, aromatic, and carboxylic acid. The liquid fraction of the pyrolysis product is alike diesel fuel. The heating value is comparable, but the values of the cetane number, flash point, viscosity, and pour point are lower than petroleum diesel (Maher and Bressler, 2007; Ogunkunle and Ahmed, 2019). Microemulsification is preparing a microemulsion of two immiscible liquids by adding surfactant to attain a thermodynamically stable dispersion. It is also termed as cosolvent blending. This method can decrease the viscosity of the oil (Ma and Hanna, 1999; Ogunkunle and Ahmed, 2019; Pereira et al., 2016). Dilution is blending vegetable oil with diesel fuel at a certain ratio to reduce its viscosity (Nguyen et al., 2010; Ogunkunle and Ahmed, 2019). On the other hand, Kusdiana and Saka (2004) have reported a method named two-step preparation of biodiesel at supercritical condition. The process involves hydrolysis of triglycerides to produce fatty acid and glycerol, followed by esterification of fatty acid with supercritical methanol to yield in FAME.

The most common method for biodiesel synthesis at the present time is through the alkaline-catalyzed transesterification of triglycerides of vegetable oils with methanol. The mechanism of transesterification comprises three steps: (1) conversion of triglyceride to 1 mole of FAME and diglyceride, (2) conversion of diglyceride to 1 mole of FAME and monoglyceride, and (3) conversion of monoglyceride to 1 mole of FAME and glycerol (Schuchardt et al., 1998).

The shortage of transesterification reaction is that this reaction produces glycerol as by-product and needs to be separated from the main product (biodiesel). Low purity of glycerol is less valuable, hence it is considered as a waste. To avoid the formation of glycerol side product, methanol can be replaced by methyl acetate or ethyl acetate (Kashyap et al., 2019). The reaction between vegetable oils with alkyl acetate, known as interesterification, will produce biodiesel and triacetin instead of glycerol. It is not necessary to separate triacetin from biodiesel product since triacetin has characteristic as fuel additive, which can improve biodiesel combustion performance form (Dhawan et al., 2020).

17.3 Interesterification reaction

The classical transesterification reaction to produce biodiesel generates glycerol as a by-product. This fact is unfavorable since it needs a set of separation process to purify biodiesel from glycerol, which consequently increases the production cost. On the other hand, the abundant product of crude glycerol causes the declining price of glycerol in the market (Kusumaningtyas et al., 2016; Lazdovica and Kampars, 2020). Therefore development of the glycerol-free process for biodiesel synthesis has grabbed a significant attention.

One attracting way to eliminate the formation of biodiesel is by using alkyl acetate as reactant instead of methanol. By substituting methanol with methyl or ethyl acetate, glycerol will not be yielded as by-product. As a substitute, the reaction between triglyceride and alkyl acetate will result in biodiesel and triacetin. The alternative route of biodiesel production using alkyl acetate as the acyl acceptor is called interesterification. This reaction can be catalyzed using enzyme, classical homogeneous catalyst such as sodium or potassium methoxide, heterogeneous catalyst, and in the absence of catalyst using supercritical condition. Metal alkoxide catalyst is among the most effective catalyst for interesterification reaction since it can result in high yield in a short time and mild condition (Lazdovica and Kampars, 2020).

In the interesterification reaction, it is unnecessary to separate triacetin, which is formed during the reaction since triacetin can blended with biodiesel as fuel additive (Casas et al., 2011; Maddikeri et al., 2014). As fuel additive, triacetin acts to improve the cetane number of the biodiesel. As the impact, it reduces the smoke emission and knocking of engine. Besides, the addition of triacetin will promote the cold properties of biodiesel. Biodiesel can be formulated with triacetin up to 10% or 20% (Lazdovica and Kampars, 2020; Maddikeri et al., 2014; Mufrodi et al., 2014).

The reaction equation of interesterification of 1 molecule of triglyceride with 3 molecules of methyl acetate results in 3 molecules of FAMEs (biodiesel) and 1 molecule of triacetine. The reaction mechanism shows that interesterification reaction is complex reaction consisting of three consecutive steps. Based on its reaction mechanism, interesterification reaction is identical to a combination of two transesterification reactions (Casas et al., 2013). In this work, interesterification between triglycerides of Jatropha oil and methyl acetate was conducted to produce biodiesel. Catalyst used in this process was sodium methoxide ($NaOCH_3$). Kinetic study was also performed in this investigation.

There are many different seed oils that can be utilized as raw material for biodiesel production. The selection of the vegetable oil depends on several factors, for instance: the locally available feedstocks, price, oil composition, technical aspect, etc. In the European Union, biodiesel is mostly prepared from rapeseed oil (Dutta, 2019; Van Duren et al., 2015). Meanwhile, soybean oil is the most dominant biodiesel feedstock in the United States (Chen et al., 2018). Waste cooking oil is also a potential feedstock in various countries (Fangfang et al., 2021). In tropical and coastal countries such as Indonesia and Malaysia, palm and coconut oil are widely applied as raw materials for biodiesel production. *Jatropha curcas* oil is also popular in Asian countries, such as India, Malaysia, and Indonesia (Anwar, 2021; Hamzah et al., 2020; Siregar et al., 2015).

Utilization of *Jatropha curcas* Linn. oil is promising since it is an nonedible oil. Hence, its utilization as bioenergy crop will not compete with the food demand (Kusumaningtyas et al., 2014). Jatropha seed has high oil content between 63.16% and 66.4%, which is higher than the oil content of palm kernel and soybean (Hamzah et al., 2020). In addition, the cetane number of Jatropha biodiesel is reported to be 57, which is comparable to diesel fuel and higher than palm biodiesel. The Life Cycle Assessment (LCA) has revealed that Jatropha biodiesel demonstrated the higher reduction value of CO_2 release from combustion than palm biodiesel (Siregar et al., 2015).

17.4 Kinetic model of interesterification reaction

Kinetic study is urgent for obtaining the kinetic parameters, which is required for the process equipment design and scaling up. However, study on the kinetics of triglyceride interesterification for biodiesel production is not widely found in literature (Brondani et al., 2020). Most findings focus on the kinetics of enzymatic interesterification, and some other discuss about the kinetics of the interesterification at supercritical condition. Kinetic analysis of the interesterification reaction using classical metal alkoxides catalyst in mild condition has not been extensively investigated. In spite of this, some research reported the compatibility of the homogeneous irreversible second-order model for this reaction (Casas et al., 2011; Teixeira et al., 2016).

Basically, interesterification consist of three sequential reversible reactions that can be described through Eqs. (17.1)–(17.3). Furthermore, the overall reaction is written in Eq. (17.4) (Casas et al., 2011):

$$TG + MA \underset{k_2}{\overset{k_1}{\rightleftarrows}} MADG + E \tag{17.1}$$

$$MAGD + MA \underset{k_4}{\overset{k_3}{\rightleftarrows}} DADG + E \tag{17.2}$$

$$DAGD + MA \underset{k_6}{\overset{k_5}{\rightleftarrows}} TA + E \tag{17.3}$$

Overall reaction:

$$TG + 3MA \underset{k_8}{\overset{k_7}{\rightleftarrows}} TA + 3E \tag{17.4}$$

Reaction rate of each compound can be written as follow [Eqs. (17.5)–(17.10)]:

$$d\frac{[TG]}{dt} = -k_1[TG][MA] + k_2[MADG][E] - k_7[TG][MA]^3 + k_8[TA][E]^3 \tag{17.5}$$

$$d\frac{[MADG]}{dt} = k_1[TG][MA] - k_2[MADG][E] - k_3[MADG][MA] + k_4[DAMG][E] \tag{17.6}$$

$$d\frac{[DAMG]}{dt} = k_3[MADG][MA] - k_4[DAMG][E] - k_5[DAMG][MA] + k_6[TA][E] \tag{17.7}$$

$$\begin{aligned} d\frac{[E]}{dt} &= k_1[TG][MA] - k_2[MADG][E] + k_3[MADG][MA] - k_4[DAMG][E] \\ &\quad + k_5[DAMG][MA] - k_6[TA][E] + k_7[TG][MA]^3 - k_8[TA][E]^3 \end{aligned} \tag{17.8}$$

$$d\frac{[MA]}{dt} = -d\frac{[E]}{dt} \tag{17.9}$$

$$d\frac{[TA]}{dt} = k_5[DAMG][MA] - k_6[TA][E] + k_7[TG][MA]^3 - k_8[TA][E]^3 \tag{17.10}$$

where TG = triglycerides, $MADG$ = monoacetin diglyceride, $DAMG$ = diacetin monoglyceride, and E = FAME (biodiesel).

Generally, the value of the reaction rate constant on the secondary group is slightly greater than that of the primary group. Since the difference constant values are not exceedingly significant, it can be assumed that the reaction, which comprises three steps occurs simultaneously. Subsequently, the overall reaction in Eq. (17.4) can be rewritten as Eq. (17.11):

$$TG + 3MA \underset{k_2''}{\overset{k_1'}{\rightleftarrows}} TA + 3E \tag{17.11}$$

The reaction rate equation can be formulated as follows [Eq. (17.12)]:

$$d\frac{[TG]}{dt} = -k_1'[TG][MA]^3 + k_2'[TA][E]^3 \tag{17.12}$$

where k_1' = reaction rate constant for the forward reaction and k_2' = reaction rate constant for the reverse reaction.

Reaction rate constant in general is defined using Arrhenius function [Eq. (17.13)]:

$$k(T) = Ae^{-E/RT} \tag{17.13}$$

where $k(T)$ = reaction rate constant, A = frequency/preexponential factor, E = activation energy (mol/J), R = ideal gas constant (8314 J/K.mol), and T = reaction temperature (K).

The units for $k(T)$ and A depend on the reaction order, namely L/mol.min and min^{-1} for the first-and second-order reactions, respectively.

Casas et al. (2011) suggested a kinetic model of irreversible interesterification of triglycerides with methyl acetate so as to Eq. (17.12) can be simplified. Once the excessive methyl acetate is employed in the reaction system, it can be assumed that forward reaction in Eq. (17.12) obeys a pseudo-first-order reaction, and the reverse reaction follows the second-order reaction law. However, when far excess methyl acetate is used in the reaction, the k value of the reverse reaction can be disregarded and supposed to be zero. For this reason, the interesterification reaction can be considered an irreversible reaction. Thus Eq. (17.12) can be simplified into a second-order irreversible reaction kinetic model as indicated in Eq. (17.14):

$$-\frac{dC_{TG}}{dt} = r_{TG} = k'.C_{TG}^2 \tag{17.14}$$

The kinetic model obtained is then presented in Eq. (17.15):

$$\frac{1}{C_{TG}} = k'.t + \frac{1}{C_{TG_o}} \tag{17.15}$$

The value of k' is affected by the catalyst concentration.

Plotting of $\frac{1}{C_{TG}}$ against t will form a linear line, denoting that the model fits the experimental data.where C_{TG} = molar concentration of triglycerides (mol/L), C_{TG_o} = initial concentration of triglycerides (mol/L), t = reaction time (min), r_{TG} = reaction rate of triglycerides (mol/L.min), and k' = reaction rate constant (L/mol.min).

17.5 Case study: kinetic study on the biodiesel synthesis from Jatropha (*Jatropha curcas* L.) with methyl acetate in the presence of sodium methoxide catalyst

In this case, Jatropha oil was obtained from PT. Jatropha Green Energi, Kudus, Jawa Tengah, Indonesia. Experimental study and kinetic reaction rate were inspected in this study. The experiment was conducted through interesterification reaction of *J. curcas* L. with methyl acetate in the presence of $NaOCH_3$ catalyst. Consecutively, kinetic factor and activation energy of interesterification reaction were obtained from the proposed kinetic model.

17.5.1 Methods

There are two main stages in this case, which are neutralization of crude Jatropha oil and interesterification of neutralized Jatropha oil. The physical and chemical properties of Jatropha oil such as density, viscosity, acid value, and acidity were analyzed before and after neutralization process.

Purification or neutralization of Jatropha oil was intended to remove the free fatty acid and avoid the gumming process in the interesterification reaction. Two hundred milliliters of crude Jatropha oil was prepared in a three-necked flask. Sodium carbonate (Na_2CO_3) was dissolved in a water with combined a mixing and heating process. Saturated Na_2CO_3 was then filtered to remove the unwanted solid and undissolved Na_2CO_3 powder. The oil was heated to 90°C, and once it reached the neutralization temperature (90°C), saturated Na_2CO_3 was injected into the oil at a low flow rate. Continuous mixing was conducted for 1 h and the solution was then separated to remove the produced soap from the oil.

$NaOCH_3$ was mixed with methyl acetate in a three-necked flask accompanied with magnetic stirrer, and the mixture was then heated to operating temperature. Purified Jatropha oil was prepared in a different apparatus and also heated to the same temperature with catalyst mixture. Once it reached the required temperature, the Jatropha oil was then poured into the previous three-necked flask, which contains catalyst and methyl acetate.

In this interesterification reaction, the catalyst concentration was varied to 0.25%, 0.5%, 0.75%, and 1%, oil to molar ratio was varied to 1:6, 1:9, 1:12, and 1:15, while the reaction time was varied to 40°C, 50°C, and 60°C. Interesterification was conducted for 8 h and the samples were taken periodically. The samples were then analyzed its composition by using gas chromatography—mass spectrometry (GC-MS).

17.5.2 Kinetic model

Triglycerides concentration from GC-MS analysis was converted into the reaction conversion. The kinetic model was then solved by using Eqs. (17.14) and (17.15), which are the proposed by Casas et al. (2011). The differential equation was solved by using Runge—Kutta method. Experimental data and the calculated triglyceride concentration were compared and calculated its sum square of error (SSE). Kinetic rate constant was determined once it reached the minimum SSE.

Kinetic factor and the energy activation were obtained by using Arrhenius equation as shown in Eq. (17.16).

$$k(T) = Ae^{-E/RT} \tag{17.16}$$

where $k(T)$ is the reaction rate constant (L/mol.min), A is the frequency/preexponential factor (L/mol.min), E is the energy activation (mol/J), R is the ideal gas constant (8314 J/K.mol), and T is the reaction temperature (K).

17.5.3 Characterization of Jatropha oil

Characteristics of Jatropha oil before and after neutralization process are demonstrated in Table 17.1. The characterization consists of oil density, viscosity, molecular weight,

Table 17.1 Physical and chemical properties of Jatropha oil.

Variable	Standard	Before	After
Density (g/mL)	0.85−0.89	0.965	0.956
Viscosity (mm^2/s)	2.3−6.0	37.83	40.39
Acid value (mg KOH/g oil)	Max 0.80	16.157	0.926
Acidity (%)	Max 0.5	8.12	0.465

acid value, and acidity. According to Table 17.1, it can be seen that neutralization process has successfully decreased all the parameters compared to the crude Jatropha oil. However, most of the parameter values are still above the required standard for diesel engine. It can be concluded that this crude oil cannot be directly used as diesel engine. Several problems that might appear when crude oil with the current physical and chemical properties is used as diesel engine are engine failure, increasing the engine weariness (Pristiyani, 2015), power loss engine (Mittlebach and Remschmidt, 2004), corrosion, and create deposit on the engine (Ferrari et al., 2011). Since the acidity value is already dropped to 0.465%, this purified Jatropha oil can be used for the next process to produce the methyl ester.

17.5.4 Effect of catalyst concentration

In this case, the concentration of $NaOCH_3$ catalyst was varied into 0.25%, 0.5%, 0.75%, and 0.1% w/w, while the other variables were remaining constant. The oil to methyl acetate molar ratio was 1:6, reaction temperature was set at 50°C, and the reaction time was 4 h. $NaOCH_3$ catalyst was chosen since it contains less water compared to sodium hydroxide (KOH) (Ma and Hanna, 1999). Based on this operating condition, the effect of catalyst concentration on the triglyceride conversion is shown in Fig. 17.2.

The result shows that higher catalyst concentration also increases the number of converted triglyceride into methyl ester. This was caused by the increasing number of available active sites to promote the reaction (Masduki et al., 2013). With the increasing number of active sites, it also reduces the energy activation and increases the reaction rate of triglyceride into methyl ester (Rasyid, 2010). Reduction on the energy activation creates more collision between the reactant particles, which can increase the reaction rate. In this case, the highest conversion was 88.1% obtained by using catalyst concentration of 1%. Maddikeri et al. (2014) in their study also reported that the optimum catalyst concentration for the interesterification of cooking oil was 1%. Higher catalyst concentration did not affect the conversion; on the other hand, it increases the catalyst recovery cost. On the previous study, Pristiyani (2015) used KOH for interesterification of used cooking oil. The results showed that the highest conversion obtained was 13.79. It can be concluded that $NaOCH_3$ is more effective as an interesterification catalyst compared to KOH.

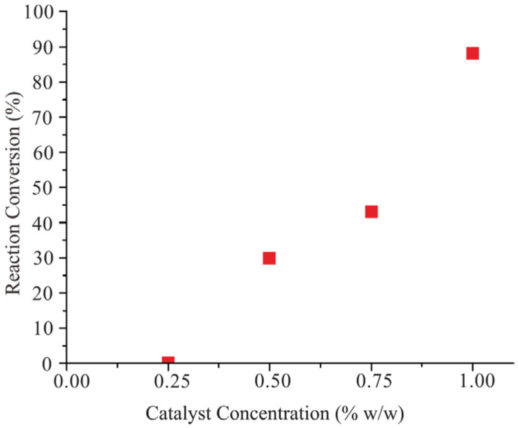

Figure 17.2 Effect of catalyst concentration on the triglyceride conversion.

Table 17.2 Methyl ester chemical compounds at the catalyst concentration of 1% w/w.

No.	Retention time, min	Area %	Chemical compound
1	43.056	0.79	Oleic acid
2	43.795	0.36	Linoleic acid
3	45.770	4.54	Methyl ester
4	49.907	10.74	Palmitic acid
5	54.825	3.14	Methyl ester
6	55.249	3.40	Mono-oleic acid
7	59.475	0.22	Methyl ester

Table 17.2 shows the chemical compounds of methyl ester by using 1% w/w of $NaOCH_3$ catalyst. It can be seen that at the current catalyst concentration and operating condition, triacetin was not found on the compounds of methyl ester although it has a quite high triglyceride conversion. Sustere and Kampars (2015) on the previous studies found that the optimum results were obtained by using catalyst to oil ratio of 0.15 with methyl acetate to oil molar ratio of 36. The catalyst used was tert-butoxide, and the product composition was 73.2% of methyl ester and 16.6% of triacetin. Since in this case the methyl ester to oil molar ratio was only 6:1, it might be the main reason triacetin was not found in the product.

17.5.5 Effect of Jatropha oil to methyl acetate molar ratio

According to the stoichiometry of interesterification reaction, 3 moles of methyl acetate is reacted with 1 mole of triglyceride. Since it is a reversible reaction, excess methyl acetate is needed to shift the reaction towards the product side (Maddikeri et al., 2014). Effect of the oil to methyl acetate molar ratio to triglyceride conversion was studied at 1:6, 1:9, 1:12, and 1:15. The reaction was conducted at reaction temperature of 50°C, catalyst concentration of 0.5% w/w, and reaction time of 4 h. Fig. 17.3 shows the effect of oil to methyl acetate molar ratio to the triglyceride conversion.

It can be seen that the conversion of triglyceride into methyl ester is decreasing along with the increasing of oil to methyl acetate molar ratio. Huang and Akoh (1996) also reported the same trend line on their study, and yield of transesterification product between triolein and caprylic acid ethyl ester was not increasing with the increasing reactant molar ratio. Moreover, excess amount of methyl ester might produce biodiesel with high viscosity and became another issue on the product separation. Reduction on the reaction conversion was caused by the low amount of triglyceride concentration, furthermore this excessive dissolution inflicted a slower reaction process. In reversible reactions such as interesterification, excess ethyl acetate might slide the equilibrium to the backward reaction, which can reduce the yield of biodiesel and triacetin (Komintarachat et al., 2015). In this case, the highest conversion was obtained at oil to methyl acetate molar ratio of 1:6 with a conversion of 29.76%. Freedman et al. (1984) previously studied the effect of molar ratio on the sunflower oil methanolysis, and the results showed that the highest ester conversion was 98% and obtained by using molar ratio of 1:6. However, ester conversion was decreased to 82% at molar ratio of 1:3.

Table 17.3 shows the chemical compounds of methyl ester obtained at oil to methyl acetate molar ratio of 1:6. Based on the GC-MS results' analysis in Table 17.3, it can be seen that with high amount of methyl ester on the product, triacetin had not been found on the product analysis. It shows that the optimization is necessary to obtain the best operating condition of the process for the future work.

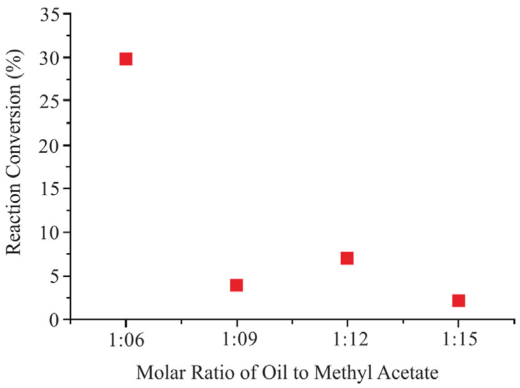

Figure 17.3 Effect of oil to methyl acetate molar ratio to the triglyceride conversion.

Table 17.3 Chemical compounds of methyl ester at molar ratio of 1:6.

No.	Retention time, min	Area %	Chemical compound
1	39.239	0.60	Palmitic acid
2	42.257	6.90	Methyl ester
3	43.108	1.10	Methyl ester
4	43.784	0.09	Stearic acid
5	45.626	6.35	Palmitic acid
6	47.695	0.05	Palmitic acid
7	47.984	0.19	Mono-oleic acid
8	48.166	0.14	Methyl ester
9	49.607	0.20	Palmitic acid
10	49.736	7.73	Methyl ester
11	51.048	0.59	Oleic acid
12	51.225	0.16	Methyl ester
13	52.843	0.46	Methyl ester
14	53.012	0.93	Methyl ester
15	53.727	0.09	Stearic acid
16	54.033	0.34	Lauric acid

17.5.6 Effect of reaction time and temperature

In this case, the reaction temperatures were varied to 40°C, 50°C, and 60°C, while the interesterification process was carried out for 8 h and samples were taken at 0, 30, 60, 120, 240, and 480 min. The remaining parameters were constant, where the catalyst concentration was 0.5% w/w and oil to methyl acetate molar ratio was 1:6. This temperature range was chosen based on the catalyst activity, which is ranged between 20°C and 100°C (Mittlebach and Remschmidt, 2004). Freedman et al. (1984) also stated that transesterification process for peanut oil, cotton seeds oil, sunflower seeds oil, and soybean seeds oil should be carried out with oil to alcohol molar ratio of 1:6, catalyst concentration of 0.5%, and reaction temperature of 60°C. Fig. 17.4 shows the effect of reaction time and temperature to the triglyceride conversion.

Triglyceride conversion is decreasing with the increasing reaction temperature. Decreasing conversion from reaction temperature of 40°C–50°C was caused by the shifted reaction equilibrium to the reactant. Interesterification reaction is an exothermic reaction, which releases energy, furthermore increasing temperature will supply more heat. According to Le Chatelier's principle, the equilibrium will shifted to the reactant side (Kusumaningtyas et al., 2014). Rachimoellah et al. (2009) reported that since transesterification is an exotherm reaction, excess methyl acetate is needed to decrease the reaction temperature and shift the equilibrium reaction to the product side. Triglyceride conversion is also decreasing on the temperature increment from 50°C to 60°C, which was due to the reaction temperature used that was higher than the boiling point of methyl acetate, which is 56.1°C (Said et al., 2010). Hence,

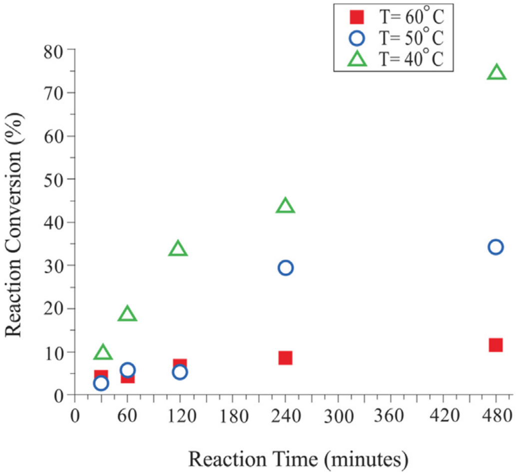

Figure 17.4 Effect of reaction time and temperature to the triglyceride converison.

reaction between oil and methyl acetate at this reaction temperature is not effective and decreases the yield of methyl ester. However, longer reaction times give more chance for the oil to react with methyl acetate and resulted in more biodiesel product. In this case, the optimum operating condition was obtained at the reaction temperature and time of 40°C and 8 h, respectively, with triglyceride conversion of 73.96%.

Chemical compounds of the product at the optimum condition are presented in Table 17.4. Based on Table 17.4, it was cleared that triacetin has not been found on the product analysis. It also can be concluded that the current operating condition was not the optimum condition for the interesterification reaction. However, glycerol was also found as the product. During the interesterification reaction between Jatropha oil and methyl acetate with KOH catalyst, the formation of triacetin di-(9-octadecenoyl)-glycerol inhibits the production of triacetin (Pristiyani, 2015). Brondani et al. (2020) suggested the higher reaction temperature and molar ratio of methyl acetate to oil in order to obtain higher yield of products.

17.5.7 Kinetic study

Fig. 17.5 shows the comparison between experimental data and the calculated triglyceride concentration as a function of reaction time and temperature. Based on the SSE between experimental data and the calculated triglyceride concentration, it can be concluded that the kinetic reaction of oil and methyl acetate interesterification process with the presence of $NaOCH_3$ catalyst can be approached by using second-order reversible kinetic model. Furthermore, based on the kinetic data for each temperature, kinetic factor (A) and energy activation (E) can be calculated by using Arrhenius equation. Table 17.5 shows the calculated kinetic rate of interesterification reaction as a function of reaction temperature.

Table 17.4 Chemical compounds of methyl ester at reaction temperature of 40°C and reaction time of 8 h.

No.	Retention time, min	Area %	Chemical compound
1	45.050	0.20	Di-9-octadecenoyl glycerol
2	45.582	4.71	Palmitic acid
3	47.952	0.13	Mono-oleic acid
4	48.129	0.11	Oleic acid
5	49.692	5.31	Methyl ester
6	53.996	4.88	Lauric acid
7	55.365	4.04	Oleic acid
8	58.987	3.40	Lauric acid
9	59.984	0.42	Lauric acid

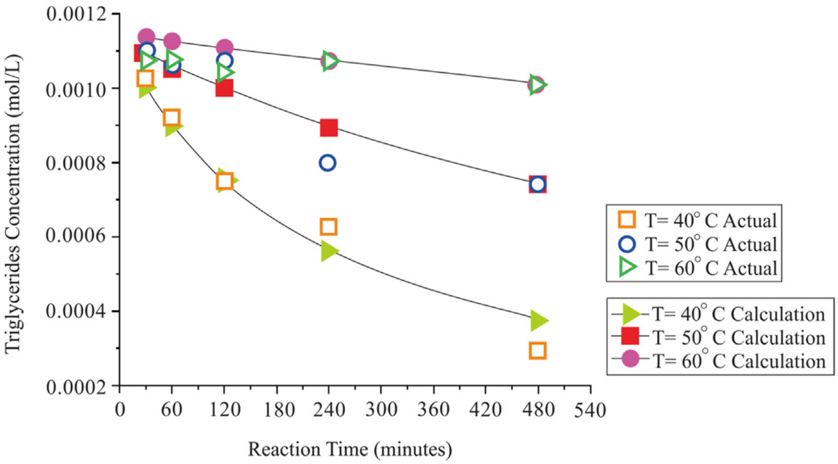

Figure 17.5 Relation between C_{TG} experimental data and C_{TG} calculated as a function of reaction time and temperature.

Table 17.5 Reaction rate constant.

Temperature (°C)	Reaction rate constant (L/mol.min)
40	1.5728
50	0.6753
60	0.2151

Regression analysis of reaction rate constant in Table 17.5 results in a preexponential factor (A) of 7.23×10^{-15} L/mol.min and energy activation in terms of $-E/R$ with 10,358 K/min. With a gas constant (R) of 8.314 J/mol/K, the obtained energy activation is 86,116.41 J/mol. Energy activation in this case was in line with the study reported by Casas et al. (2011), where the energy activation for conventional interesterification process was between 24,318 and 88,551 J/mol. The results are in accordance with Le Chatelier's principle, where reaction equilibrium will shift to the reactants for an exothermic reaction. As it can be seen in Table 17.5, the reaction rate is decreasing along with the increasing reaction temperature.

17.6 Conclusion

The data presented in this work demonstrate the feasibility of producing biodiesel fuels through interesterification reaction of Jatropha oil with methyl acetate in the presence of $NaOCH_3$ catalyst. Various parameters were studied, and it shows that the highest yield obtained in this study was 88.1% in oil to methyl acetate molar ratio of 1:6, reaction temperature of 50°C, and catalyst concentration of 1% w/w with 4 h of reaction time. Hence, highest catalyst concentration still can be used to achieve higher triglyceride conversion. Moreover, the resultant analysis of biodiesel product from various operating conditions shows the absence of triacetin. The kinetic model was fitted with the second-order reaction kinetic model. The energy activation was in line with the previous studies, which was 86,116.41 J/mol, while the preexponential factor (A) was 7.23×10^{-15} L/mol.min.

Acknowledgment

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