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Production of Biokerosene Hydrocarbons using Coconut Oil with CoO-NiO/Kaolin Catalyst via Solvent-free and Inert Atmosphere Catalytic Deoxygenation

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ABSTRACT

Concerns on the depletion of fossil fuel and emissions of harmful gases lead to the search for alternative aviation fuel. The present study demonstrates the production of biokerosene hydrocarbons from coconut oil via solvent-free catalytic deoxygenation under inert Nitrogen (N_2) atmosphere. The deoxygenated product is examined through Gas Chromatography-Mass Spectrometry (GC-MS) analysis to determine its chemical composition and hydrocarbons distribution. CoO-NiO/Kaolin catalyst was used along with several other catalysts to study the reactivity of different catalysts in catalytic deoxygenation. Coconut oil is composed of middle-chain saturated fatty acids (capric acid, lauric acid, and myristic acid) which are favorable for the conversion into biokerosene hydrocarbons due to their carbon chain length. In terms of the types of catalyst, CoO-NiO/Kaolin proves to be the best catalyst with optimum selectivity of biokerosene hydrocarbons at 83.4%. A parametric study was executed on coconut oil using CoO-NiO/Kaolin, and the result indicated that the optimum reaction conditions are 330 °C, 2 hours of reaction time, and 5 wt.% of catalyst. The biokerosene hydrocarbons produced have the likelihood to be the drop-in substitutes for aviation fuel.

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1. INTRODUCTION

The aviation industry is a popular sector, and the world aircraft fleets are forecasted to be 33,070 aircraft in 2035 [1]. The aviation industry growth heightens fossil fuel consumption, leading to fossil fuel depletion. The industry's rapid growth also exacerbated the climate change associated with greenhouse gas emissions from aviation fuel combustion. The emissions from both passenger and cargo carriages are reported to be 2.4% of the estimated 37.9 gigatons of total carbon dioxide emitted globally from fossil fuel use in 2018 and have increased over the years [2]. The CO_2 emissions from commercial flights have increased 32% over the past five years from the 694 MMT emitted in 2013 [3]. The International Air Transport Association (IATA) and the International Civil Aviation Organization (ICAO) have identified the development of biofuel as one of the four pillar strategies to combat the climate change problem [4]. The utilization of sustainable biofuel reduces lifecycle carbon dioxide emissions by 50% to 80% compared to petroleum fuel as reported by the US Department of Energy [3]. As an effort to mitigate the emissions of carbon dioxide, reduces carbon dioxide lifecycle, and overcome the depletion of fossil fuels, studies on alternative aviation fuel or also known as biokerosene are actively conducted globally.

Kerosene type fuel is a standard worldwide aviation fuel for passenger and cargo aircrafts. It is made up of hydrocarbons with the carbon chain length between C6 and C15 derived between diesel and petrol from crude oil distillate. In search of sustainable biokerosene, various plant oil feedstocks consisting of triglycerides for the production of biokerosene have been studied by past researchers [5]–[18]. Triglyceride is composed of long-chain fatty acid esters that build up the chemical structure of vegetable oil and animal fats [19]. The carbon-hydrogen-oxygen bonded fatty acid structure is almost similar to the crude oil's hydrocarbon chain content. There are several pathways for the conversion of plant oils into biofuel such as pyrolysis [13], transesterification [5], [8], [18], [20], [21], and hydrodeoxygenation (HDO) [17], [22]–[24]. The fatty acid methyl esters (FAME) obtained from transesterification method have several disadvantages such as high viscosity, high pour point, high acid number, low heat value, and low stability which are attributed by the oxygenated compounds in FAME [25]–[28].

Meanwhile, the HDO of triglycerides through the hydrogenolysis method requires a vast amount of hydrogen gas and expensive catalyst, resulting in less environmental-friendly and less economical for extensive applications [29]–[31]. Another method that has received much attention in recent years as a feasible conversion route is catalytic deoxygenation (DO) method. The DO reaction eliminates the oxygen component from the fatty acids. It produces mostly linear hydrocarbons with a high atomic ratio of hydrogen to carbon (H/C) and a low atomic ratio of oxygen to carbon (O/C) [32], [33]. Such composition contributes to greater energy content in the fuel [34], better oxidation stability [35], and a high cetane number [36]. Recent years have shown several studies applying the deoxygenation method to convert jatropha [37], waste cooking oil [38], and other feedstocks to diesel range hydrocarbon fuel [39], [40]. However, there has been little discussion on the application of the deoxygenation method in converting various feedstocks into clean alternative aviation fuel or biokerosene hydrocarbon fuel. This paper aims to study the feasibility of deoxygenation in producing biokerosene hydrocarbon fuel using feasible feedstock and inexpensive catalysts.

Over the past few years, several catalysts have been studied for the deoxygenation and cracking of fats and oils into hydrocarbon-like fuel. The commercially available catalysts are comprised of noble metals which are Pd and Pt. These noble metals have shown great performance in converting fats and oils into hydrocarbon-like fuel. However, the expensive cost related to noble metal catalysts has driven the search for other inexpensive catalysts using earth-abundant metals. One of the metals that have gained attention is Ni due to its comparable performance to Pt and Pd with certain feeds and reaction conditions during deoxygenation activity [41]. In this study, the performance of several inexpensive metal catalysts will be investigated to determine the best catalyst for the deoxygenation of plant oils into hydrocarbon-like fuel.

2. METHODOLOGY

2.1 Materials

Coconut oil was procured from a local supermarket. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) were obtained from HmbG Chemicals. Kaolin was purchased from Qrec and silica-alumina (SiO_2-Al_2O_3) catalyst support grade 135 was obtained from Sigma Aldrich. Three other catalysts: $ZnO/Al_2/O_3$, CaO/Al_2O_3, and ɣ-CaO/Al_2O_3 were purchased from the Department of Chemistry, Universiti Teknologi Malaysia. N-Hexane solvent (GC grade) with purity >98% from Merck was used for dilution purposes.

2.2 Catalyst synthesis

Several catalysts were synthesized and used in the DO method to determine the best catalyst for biokerosene production. Kaolin supported CoO-NiO catalyst was synthesized via wet impregnation method whereby an aqueous solution of 10g of Kaolin was impregnated with aqueous solutions of 10 wt.% of Co and 10 wt. % of Ni. The mixture is then stirred for 6 hours at ambient temperature and then dried in a vacuumed rotary evaporator for 3 hours. The dried samples were then grounded into fine powder and subsequently thermally activated in a furnace at a temperature of 700 ^oC for 3 hours under atmospheric pressure. Meanwhile, NiO-CaO_5/SiO_2-Al_2O_3 catalyst was synthesized via the impregnation method according to conditions described in a study by N.Asikin-Mijan et al. [31]. Three other catalysts: $ZnO/Al_2/O_3$, CaO/Al_2O_3, and ɣ-CaO/Al_2O_3 were purchased from the Department of Chemistry, Universiti Teknologi Malaysia..

2.3 Deoxygenation reaction

The deoxygenation reaction was performed in a flat bottom flask placed on a hot plate with a magnetic stirrer, as shown in Figure 1. Feedstock (coconut oil) was introduced into the flat bottom flask and 5 wt. % of the catalyst was added into the flat bottom flask. The flask content was flushed with Nitrogen (N_2) gas for 5 minutes to remove other gases. The DO reaction is started by heating the reaction medium to 330 ^oC under inert condition (flowing N_2) for 2 hours. The generated vapour was then condensed into liquid product as it passed through the condensation column and finally, the deoxygenated product was collected in the receiver flask. The deoxygenated product is identified as biokerosene.

All the experiments are carried out at the Gas Turbine Combustion Research Laboratory in the School of Mechanical Engineering, Universiti Teknologi Malaysia.

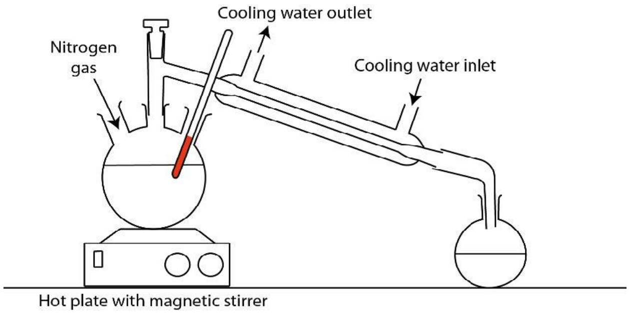

Figure 1 Experimental setup for deoxygenation reaction

2.4 Analysis of deoxygenated product

Chemical composition of the deoxygenated product was qualitatively and quantitatively analyzed using gas chromatography-mass spectrometry (GC-MS Model Agilent 7697A). The deoxygenated product is first diluted with GC-grade n-hexane prior to the analysis. Helium gas served as the carrier gas, and the initial temperature of the oven was set to 70 °C and held for 10 minutes, and then ramped up to 300 °C at the heating rate of 5 °C/min. The generated peaks representing the compounds were identified using National Institute of Standards and Testing (NIST) database. The hydrocarbon (HC) yield was determined using the equation below:

$$HC\ Yield\ (\%) = \frac{\sum n_o + \sum n_i}{\sum n_z} \text{ x } 100\%$$

where n_o = total area of alkene (C_6 to C_{15}), n_i = total area of alkane (C_6 to C_{15}), n_z = total area of the product.

3. RESULTS

3.1 Catalytic activity and deoxygenation product

Plant oils with medium-chain fatty acids are favored for biokerosene production as it is close to kerosene fuel in terms of carbon number, therefore coconut oil was identified as the most attractive feedstocks. It can be observed that the percentage of hydrocarbons acquired from the DO reaction of coconut oil is high (83.4%) which could be ascribed to the composition of coconut oil, which is majorly composed of medium-chain saturated fatty acids like capric acid (C10:0), lauric acid (C12:0), and myristic acid (C14:0) as shown in Table 1. The composition of fatty acids and the degree of saturation is essential in determining the reaction pathways that will undertake and subsequently influence the formation of the deoxygenated products. This is because the unsaturated fatty acid may induce coke formation and simultaneously reduce deoxygenation activity [6].

Table 1 Fatty acid compositions of coconut oil

Components (%)	Coconut oil [42]
Caproic acid (C6:0)	0.52
Caprylic acid (C8:0)	7.6
Capric acid (C10:0)	5.5
Lauric acid (C12:0)	47.7
Myristic acid (C14:0)	19.9
Palmitic acid (C16:0)	-
Stearic acid (C18:0)	2.7
Oleic acid (C18:1)	6.2
Linoleic acid (C18:2)	1.6
Arachidic acid (C20:0)	-
Eikosenoic acid (C20:1)	-

In the present study, CoO-NiO/Kaolin catalyst was synthesized via wet impregnation method to determine the catalyst's reactivity in the deoxygenation experiment. A comparison between CoO-NiO/Kaolin catalyst with several other catalysts was made in this study. The catalytic activity of the catalysts represented by the percentage of hydrocarbons in the deoxygenated product is displayed in Figure 2. The highest biokerosene hydrocarbon yield was observed when using CoO-NiO/Kaolin catalyst with 83.4% of hydrocarbons. Meanwhile, NiO-CaO_5/SiO_2-Al_2O_3 catalyst reactivities were 55.6%. Analysis of the hydrocarbon yield for the DO of coconut oil indicates that the reactivity of all the catalysts is in the order of CoO-NiO/Kaolin (83.4%) > NiO-CaO_5/SiO_2-Al_2O_3 (55.6%) > ZnO/Al_2O_3 (49.3%) > CaO/Al_2O_3 (35.8%) > ɣ-CaO/Al_2O_3 (25.2%). The other three catalysts with only 1 supported metal (ie. ZnO, CaO, and ɣ-CaO) show lower hydrocarbon yields. This could be attributed to the availability of only one support metal in comparison with the bimetallic catalysts with two supported metals (ie. CoO-NiO and NiO-CaO_5). It can be concluded that bimetallic catalysts outperform monometallic catalysts. A bimetallic catalyst enables surface-catalyzed reactions to occur over two distinct types of active sites concurrently. This could explain the higher yield obtained by bimetallic catalysts CoO-NiO/Kaolin and NiO-CaO_5/SiO_2-Al_2O_3. The result shows that CoO-NiO performs better in deoxygenation reaction with 83.4% yield as compared to only 55.6% of yield by NiO-CaO_5. Both catalysts are using Ni as one of the active metals since Ni has repeatedly proven to be comparable with the noble metal catalyst. In the present work, the Co-Ni formulation resulted in higher catalyst activity and selectivity compared to Ca-Ni formulation. In contrast to the yield obtained in this study, original work by N.Asikin-Mijan et al. [31] on deoxygenation of jatropha oil using NiO-CaO_5/SiO_2-Al_2O_3 catalyst has successfully produced 73.3% of straight-chain C8 to C20 hydrocarbons under the optimum reaction condition of 340 °C, 7 wt.% of catalyst within 60 mins of reaction. This could be attributed to the fact that these authors had performed the reaction in a 0.1 mbar pressurized reactor which further assist in the conversion of triglycerides into hydrocarbons. Lower hydrocarbon yield using the same catalyst observed in the present study could be attributed to the lower catalyst amount (5 wt.%), lower temperature (320 oC), and atmospheric pressure environment. In addition to that, the present study only considers carbon chains in the range of C6 to C15 for biokerosene, whereas the previous study considers wider carbon chains between C8 up to C20 for green diesel.

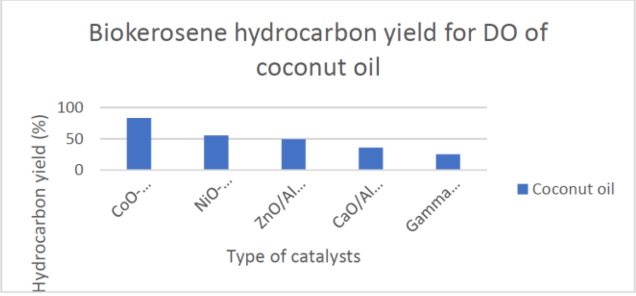

Figure 2 Biokerosene hydrocarbon yield for different types of catalysts

Detailed analysis of the deoxygenated product using CoO-NiO/Kaolin catalyst was carried out to explore the possible reaction pathways that occurred during the reaction.

Figure 3 displays the hydrocarbon distribution for coconut oil. A distinct peak of C13 hydrocarbons can be observed with a prime composition of 40.20%, followed by 15.55% of C11 hydrocarbons. The hydrocarbons produced by CoO-NiO/Kaolin contain one less carbon atom than the fatty acids. Kaolin as a support material provides significant upgrading properties at moderate reaction temperature due to its nature of moderate acidity. Moderate acidity catalyst support is favored because high acidity can cause cracking of the generated n-alkanes and therefore, reduces its selectivity [43]. In addition to that, the incorporation of two or more metals modifies the active sites and consequently there are less tendency to catalyst deactivation, reduces cracking, and promotes alkane yield by synergism [43]. Meanwhile, both Co and Ni are attractive due to its excellent catalytic performance and lower cost. Higher catalyst selectivity (>90%) in relation of oxygen-free products were previously observed when Co was used as promoter [44]. It was concluded previously that both Ni and Co active metals promotes the synergistic effect and consequently, forms a range of n-C_7 to n-C_{18} alkanes which are in the intended range of kerosene [43]. In fine, it can be inferred that this catalyst is capable of cracking triglycerides. The predominant reaction pathway of the deoxygenation catalyzed by CoO-NiO/Kaolin is decarboxylation. Decarboxylation refers to the formation of n-alkanes with one less carbon atom than the original fatty acids composition by removing the O_2 from the fatty acids [10]. This could be due to Co metal in the catalyst which favored the decarboxylation reaction pathway. However, deoxygenation under an inert atmosphere (in the absence of H_2) via the decarboxylation route only occurred to a limited extent while the predominant reaction pathways are cracking, oligomerization, aromatization, and cyclization [45].

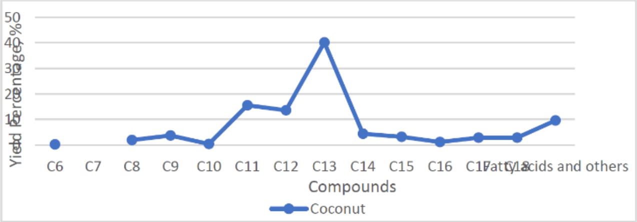

Figure 3 Hydrocarbons distribution in the deoxygenated product using CoO-NiO/Kaolin catalyst

4. CONCLUSION

Solvent-free catalytic deoxygenation of fatty acids from coconut oil for biokerosene hydrocarbons production has been performed under inert N_2 atmosphere. Coconut oil was chosen due to its fatty acids composition, which is made up of middle-chain fatty acids such as capric acid (C10), lauric acid (C12), and myristic acid (C14). These fatty acids are close to kerosene-range C6 to C15 hydrocarbons, making the coconut oil attractive as biokerosene feedstock. Aiding the deoxygenation reaction, CoO-NiO/Kaolin catalyst has been synthesized and used along with several other catalysts. The deoxygenated products were investigated by GC-MS analysis to determine the hydrocarbons distribution. The results of biokerosene hydrocarbons yield indicated that the reactivity of the catalysts is in the order of CoO-NiO/Kaolin (83.4%) > NiO-CaO_5/SiO_2-Al_2O_3 (55.6%) > ZnO/Al_2O_3 (49.3%) > CaO/Al_2O_3 (35.8%) > ɣ-CaO/Al_2O_3 (25.2%). Further analysis of the hydrocarbon's distributions using CoO-NiO/Kaolin showed that coconut oil is capable of producing biokerosene with major components of C11 to C13. Through parametric study, the optimum reaction conditions were reported to be 330 ^{o}C, 2 hours reaction time, and 5 wt.% of catalyst. Biokerosene hydrocarbon is a promising alternative as drop-in aviation fuel.

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REFERENCES

[1] A. Mega, A. Chief, and C. Officer, 33 (2019) 4–5.
[2] B. Graver, K. Zhang, and D. Rutherford, Work. Pap. (2019) 13.
[3] IATA, IATA 2015 Report on Alternative Fuels Edition 10th (2016).
[4] V. R. Banbury, John; Behrens, David; Bowell, Quentin; Campos, Norma; Cirilo, Carlos; Choi, Taeyun P; Dufresne, Stephane; Hollingsworth, Peter; Markou, Chris; Mavris, Dimitri; Pinon, Olivia; Raczynski, Chris; Roetger, Thomas; Sung, WoongJe; Toepoel, Vincent RBan, "The IATA Technology Roadmap Report, (2009).
[5] A. Llamas, M. J. García-Martínez, A. M. Al-Lal, L. Canoira, and M. Lapuerta, Fuel. 102 (2012) 483–490.
[6] L. N. Silva, I. C. P. Fortes, F. P. De Sousa, and V. M. D. Pasa, Fuel. 164 (2016) 329–338,.
[7] C. A. Scaldaferri and V. M. D. Pasa, Chem. Eng. J. 370 (2019) 98–109.
[8] N. Saifuddin, A. Siti Fazlili, P. Kumaran, N. Pei-Jua, and P. Priathashini, IOP Conf. Ser. Earth Environ. Sci. 32 (2016).
[9] C. J. Chuck and J. Donnelly, Appl. Energy. 118 (2014) 83–91.
[10] S. Khan, A. N. Kay Lup, K. M. Qureshi, F. Abnisa, W. M. A. Wan Daud, and M. F. A. Patah, J. Anal. Appl. Pyrolysis. 140 (2019) 1–24.
[11] J. Yang, Z. Xin, Q. (Sophia) He, K. Corscadden, and H. Niu, Fuel. 237 (2019) 916–936.
[12] D. Chiaramonti, M. Prussi, M. Buffi, and D. Tacconi, Appl. Energy. 136 (2014) 767–774.
[13] D. Chiaramonti, M. Buffi, A. M. Rizzo, G. Lotti, and M. Prussi, Biomass and Bioenergy. 95 (2016) 424–435.
[14] M. Anand et al., Fuel Process. Technol. 151 (2016) 50–58.
[15] V. Itthibenchapong, A. Srifa, R. Kaewmeesri, P. Kidkhunthod, and K. Faungnawakij, Energy Convers. Manag. 134 (2017) 188–196.
[16] A. S. Auzani, April, 2020.
[17] Y. Scharff, D. Asteris, and S. Fédou, OCL - Oilseeds fats, Crop. Lipids. 20 (2013) 2–5.
[18] L. N. Silva, C. C. Cardoso, and V. M. D. Pasa, Fuel. 166 (2016) 453–460, 2016.
[19] R. Myers, Choice Rev. Online. 41, no. 06, pp. 41-3456-41–3456, 2004.
[20] A. Suryanto, S. Suprapto, and M. Mahfud, Mod. Appl. Sci. 9 (2015) 93.

[21] D. Sahu, D. Shetty, R. Kumar, and S. Bekal, 5 (2015) 19–27.
[22] R. Sotelo-Boyas, F. Trejo-Zarraga, and F. de Jesus Hernandez Loyo, Hydrogenation (2012).
[23] D. Verma, B. S. Rana, R. Kumar, M. G. Sibi, and A. K. Sinha, Appl. Catal. A Gen. 490 (2015) 108–116.
[24] H. Wang and S. K. Y. S. S. O. Ng, 3504165 (2012) 134.
[25] C. Yang, R. Nie, J. Fu, Z. Hou, and X. Lu, Bioresour. Technol. 146 (213) 569–573.
[26] Y. Yang, Q. Wang, X. Zhang, L. Wang, and G. Li, Fuel Process. Technol.116 (2013) 165–174.
[27] Y. Yang, J. Chen, and H. Shi, Energy and Fuels. 27, (2013) 3400 3409.
[28] S. Ahmed, M. H. Hassan, M. A. Kalam, S. M. Ashrafur Rahman, M. J. Abedin, and A. Shahir, J. Clean. Prod. 79 (2014) 74–81.
[29] N. Asikin-Mijan et al., J. Anal. Appl. Pyrolysis. 120 (2016) 110-120.
[30] C. H. Ko, S. H. Park, J. K. Jeon, D. J. Suh, K. E. Jeong, and Y. K. Park, Korean J. Chem. Eng.29 (2012) 1657–1665.
[31] N. Asikin-Mijan, H. V. Lee, Y. H. Taufiq-Yap, G. Abdulkrem Alsultan, M. S. Mastuli, and H. C. Ong, Energy Convers. Manag. 141 (2017) 325–338.
[32] C. S. Inc., Study of Technologies to Convert Biodiesel to Hydrocarbon Fuels, 2013.
[33] S. Karatzos, J. S. van Dyk, J. D. McMillan, and J. Saddler, Biofuels, Bioprod. Biorefining. 11 (2017) 344–362.
[34] M. J. A. Romero, A. Pizzi, G. Toscano, G. Busca, B. Bosio, and E. Arato, Waste Manag. 47 (2016) 62–68.
[35] G. Knothe, Energy Environ. Sci. 2 (2009) 759–766.
[36] Y. Içingür and D. Altiparmak, Energy Convers. Manag. 44 (2003) 389–397.
[37] N. Asikin-Mijan, H. V. Lee, G. Abdulkareem-Alsultan, A. Afandi, and Y. H. Taufiq-Yap, J. Clean. Prod. 167(2017) 1048–1059.
[38] A. Alsultan, A. Mijan, and T. Yap, Mater. Sci. Forum, 840 (2016) 348–352, 2016.
[39] M. Snåre, I. Kubičková, P. Mäki-Arvela, K. Eränen, J. Wärnå, and D. Y. Murzin, Chem. Eng. J. 134 (2007) 29–34.
[40] I. Simakova, O. Simakova, P. Mäki-Arvela, A. Simakov, M. Estrada, and D. Y. Murzin, Appl. Catal. A Gen. 355 (2009) 100–108.
[41] T. Morgan, D. Grubb, E. Santillan-Jimenez, and M. Crocker, Topics in Catalysis. 53(2010) 820–829.
[42] J. Orsavova, L. Misurcova, J. Vavra Ambrozova, R. Vicha, and J. Mlcek, Int. J. Mol. Sci. 16 (2015) 12871–12890.
[43] A. Galadima and O. Muraza, Journal of Industrial and Engineering Chemistry, vol. 29 (2015)12-23.
[44] N. Arun, R. V. Sharma, and A. K. Dalai, Renewable and Sustainable Energy Reviews. 48 (2015), 240-255.
[45] R. W. Gosselink et al., ChemSusChem. 6 (2013) 1576–1594.