Energimyndighetens titel på projektet – svenska Från skog till låga växthusgasstrålebränslen med en utvecklad katalytisk pyrolysteknik	
Energimyndighetens titel på projektet – engelska From forest to low GHG jet biofuels by a developed catalytic pyrolysis technology	
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Nyckelord: 5-7 st Catalytic hydropyrolysis; Biomass; Structure-modified zeolites; Hierarchical HBeta; Guard catalyst; Hydroconversion catalyst; Renewable jet fuel components	

Preface

The above-mentioned project has been financed by the Swedish Energy Agency (Energimyndigheten) via the research program "Forskning och innovation för ett hållbart och biobaserat samhälle (Bio+)". It was a joint project between RISE and LTU.

Content

Sammanfattning

Aromatiska kolväten är viktiga komponenter i flygbränslen, främst på grund av deras egenskaper att sänka fryspunkten, förbättra smörjförmågan och förhindra bränsleläckage i motorer och bränslesystem genom interaktioner med polymertätningarna. Om dessa kolväten produceras från fossila resurser bidrar konsumtionen av flygbränsle till ökande CO2 nivårer i atmosfären. Därför är en effektiv användning av förnybara resurser, såsom biomassa, för att producera flygbränslekomponenter ett viktigt steg mot att bygga ett hållbart samhälle. Strukturmodifierade zeolitkatalysatorer, som möjliggör en högselektiv produktion av aromatiska kolväten för flygbränslen från biomassa via katalytisk pyrolys, syntetiserades och utvecklades i ett PyroGC-MS/FID-system. De strukturmodifierade katalysatorerna av hierarkisk HBeta (HRCHY HBeta) kristaller och defektfria nano kristaller av ZSM-5 (ZSM-5-F) användes för att selektivt deoxygenation reaktiva ämnen i pyrolysångor från biomassa, vilket resulterade i ett högt utbyte av förnybara flygbränslekomponenter (bioflygbränslen; BJFs). Zeoliternas morfologi utformades för att förbättra diffusionen av pyrolysångorna och de uppgraderade produkterna, i katalysatorn, för att selektivt producera BJF-kolväten. Projektet syftade också till att utveckla katalysator- och teknologidesign för att selektivt omvandla biomassa till BJF-komponenter via en ex-situ katalytisk hydropyrolysprocess. Utformningen av katalysatorkonfigurationen genomfördes med hänsyn till att en effektiv katalysator för biomassapyrolysprocessen kräver: (i) en förhöjd diffusionshastighet för reaktanter/produkter till och från katalysatorns aktiva platser, (ii) hämmande av oönskade reaktioner, och (iii) förebyggande av deaktiveringsmekanismer. Därför användes en bädd av väldesignad krackningskatalysator (HRCHY HBeta), följt av en lämplig hydrokonverteringskatalysator (Mo/TiO2), för att selektivt pyrolysera sågspån till BJF. Den nya katalysatordesignen kombinerades med en skräddarsydd kontinuerlig falltubspyrolysator för att producera högkvalitativ bioolja. HRCHY HBetas morfologi utformades specifikt för att förbättra selektiviteten mot aromatiska kolväten i intervallet för flygbränslekemikalier, samtidigt som diffusionshastigheten för pyrolysångor och uppgraderade produkter genom katalysatorns kanaler och porer förbättrades. Effekterna av olika processfaktorer, såsom struktur och morfologi av HRCHY HBeta, processtemperatur över katalysatorn, gasmiljö i reaktorn, koncentration av HRCHY HBetas aktiva platser och katalysatorernas beständighet, på processeffektiviteten med avseende på reaktionsselektivitet mot BJF, värmevärdet hos pyrolysprodukterna och koleffektiviteten för hela processen undersöktes.

Summary

Aromatic hydrocarbons are important components of jet fuels mainly due to their effects on lowering the freeze point, enhancing the lubricity, and preventing the fuel leakage in the engines and fueling systems by interacting with their polymer seals. Produced from fossil resources, jet fuel consumption contributes to rising atmospheric CO_2 levels. Therefore, efficient utilization of renewable resources, such as biomass, to produce jet fuel components is an important step toward building a sustainable society. Hence, structure-modified zeolite catalysts that determine a high selective production of aromatic hydrocarbons in the range of jet fuel chemicals from biomass via catalytic pyrolysis were synthesized and engineered in a PyroGC-MS/FID system. The structure-modified catalysts of hierarchical HBeta (HRCHY HBeta) and defect-free nano-sized crystals ZSM-5 (ZSM-5-F) were used to selectively deoxygenate the reactive species in biomass pyrolysis vapors leading to a high production of renewable jet fuel components (bio

jet fuels; BJFs). The morphology of zeolites was designed for an enhanced diffusion of biomass pyrolysis vapors and upgraded products, in and out of the catalyst, to selectively produce BJF hydrocarbons. This project also aimed to develop catalyst and technology design to selectively convert biomass into BJF components via ex-situ catalytic hydropyrolysis process. Design of catalyst configuration was carried out considering the fact that an efficient catalyst for biomass pyrolysis process requires (i) an improved diffusion rate of reactants/products to and from the catalyst active sites, (ii) suppression of secondary reactions, and (iii) prevention of deactivation mechanisms. Hence, a bed of a well-designed cracking catalyst (HRCHY HBeta) followed sequentially by a suitable hydroconversion catalyst (Mo/TiO_2) was used to selectively pyrolyze the sawdust into BJFs. The new catalyst design was coupled with a customized continuous drop tube pyrolyzer to produce high-quality bio-oil. The morphology of HRCHY HBeta was specifically designed to enhance the selectivity towards aromatic hydrocarbons in the range of jet fuel chemicals, while improving the diffusion rate of biomass pyrolysis vapors and upgraded products through the catalyst channels and pores. Effects of different process factors, such as structure and morphology of HRCHY HBeta, catalyst upgrading temperature, pyrolysis gas environment, concentration of HRCHY HBeta active sites, and durability of catalysts, on the process efficiency concerning reaction selectivity towards BJFs, heating value of the pyrolysis products, and carbon efficiency of the whole process were investigated.

Introduction/Background

Due to the continuous depletion of fossil resources and detrimental effects of their utilization on environment, the continuous increasing energy and materials demand has directed the research efforts to find alternative renewable resources. Lignocellulosic biomass presents a potential promising alternative as it can be converted into fuels and range of special chemicals through thermochemical conversion processes, such as fast pyrolysis as one of the promising techniques. Bio-oils produced from biomass pyrolysis are incompatible with current jet fuel engines and fuel infrastructure due to its complex structure consisting of more than 400 different organics (e.g., phenols, acids, ketones, aldehydes, alcohols, furans, and carbohydrates) [1-3], necessitating its further upgrading for being used as fuel in the current transportation systems, such as aviation industry. The pyrolysis liquid can be upgraded to transform these oxygenates into aromatic and aliphatic hydrocarbons (HCs) in the range of jet fuels via either upgrading of the downstream pyrolysis liquid or upgrading of the pyrolysis vapors avoiding the post treatment of the downstream pyrolysis liquid [2, 4, 5]. For upgrading of pyrolysis vapors in one-step process, application of catalyst as in-situ or ex-situ configuration is necessarily needed. In in-situ catalytic pyrolysis, the feedstock and catalyst are mixed in the pyrolysis reactor, whereas in ex-situ upgrading the catalytic reactor is placed separately downstream of pyrolyzer in flow stream. Catalytic hydropyrolysis is an efficient process to improve the quality of biomass pyrolysis liquid for higher selectivity towards components in the range of jet fuel hydrocarbons (C8─C18 aromatics and aliphatics).

So far, different types of catalysts have been used for pyrolysis vapors upgrading which among them zeolites have been widely investigated due to their abilities in better facilitating the desired upgrading reactions (e.g., dehydration, decarbonylation, decarboxylation, and aromatization), reducing the oxygenates and consequently increasing the aromatic hydrocarbons. Zeolites are ordered microporous materials that are well-known catalysts for gas-phase upgrading reactions in petrochemical and refining processes [6, 7]. However, the overall yield of the upgraded pyrolysis liquid is low, and the catalyst is readily deactivated due to coke formation and excessive cracking to non-condensable gases [6, 8-10]. Producing bio jet fuel (BJF) chemicals using these versatile catalysts requires a novel approach to the current state-of-the-art. The extent of occurrence of upgrading reactions mainly depend upon the diffusion of pyrolyzates into zeolite catalyst pores, internal volume of pores and diffusion of products out of the pores. Thus, pore structure and surface chemistry of zeolite catalysts, especially the Bronsted acid sites on both internal and external sides, are the important characteristics for high selectivity of HCs production with limited formation of undesired oxygenates [11, 12].

The morphology of microporous zeolite catalysts can be specifically designed for enhanced diffusion of pyrolysis vapors and upgraded products, in and out of the catalyst, to produce stable hydrocarbons at high yields. An efficient catalytic fast pyrolysis process requires (i) an improved diffusion rate of reactants/products to and from the catalyst active sites, (ii) suppression of secondary reactions, and (iii) prevention of deactivation mechanisms. Zeolites modification especially the pores structure/shape selectivity and acidic sites (Si/Al ratio) can be adjusted to improve their performances for pyrolysis vapors upgrading. Perceiving the significant effects of shape selectivity and acidic sites of zeolite catalysts on aromatic HCs yield from pyrolysis vapors upgrading, these catalysts depending upon type of feedstock and other pyrolysis conditions, can be further modified for optimum production of monoaromatic HCs in the range of jet fuel chemicals.

In this project, structure-developed zeolite catalysts with improved mass transfer were prepared based on defect-free nanocrystals (ultra-thin ZSM-5-F catalyst) and/or using desilication technique to create mesoporous/hierarchical morphologies (HRCHY HBeta). The relationship between structure and activity of zeolite catalysts for upgrading the pyrolysis products from Sweden's forestry residues were studied. The effect of pyrolysis configurations (in-situ and ex-situ catalytic modes) on the process efficiency was investigated. This study aimed to find the connection between catalyst and biomass feedstock properties for selective proceeding of pyrolysis reactions toward BJFs formation using analytical pyrolysis. In addition, the ultra-thin ZSM-5-F catalyst was tested in a continuous system to convert a representing biomass pyrolysis oil sample, consisting of syringol, guaiacol, methanol, and water, into hydrocarbons in the range of jet fuel chemicals (C8–C18). This study aimed also to develop an efficient single-step fast pyrolysis process for selectively converting sawdust into BJF components. Hence, the structure-modified Beta zeolite in combination with hydroconversion catalyst of Mo/TiO_2 (metal-acid bifunctions) was used to improve the overall mass transfer and catalytic performance in the conversion of sawdust into BJFs via atmospheric hydropyrolysis process.

Project Execution

This project focused on experimental investigation of catalytic pyrolysis/hydropyrolysis in micro- to bench-scales, focusing on the conversion of forestry residues into bio jet fuel components. For the primary pyrolysis tests, the home-made catalysts of ultra-thin defect-free ZSM-5 (ZSM-5-F) and hierarchical HBeta (HRCHY HBeta) were prepared by LTU and RISE employing respectively the strategies (i) making the zeolite particles nanosized with an optimized morphology using biopolymers as dispersing agent and (ii) generating multiple levels of porosity within the HBeta structure. Elemental, N_2 adsorption-desorption, SEM-EDS, TPD and XRD analysis were performed to determine the properties of the catalysts (WP1). At RISE, analytical pyrolysis of two different forestry waste biomass (sawdust of pine and spruce mixture as well as a forest residue fraction named grot, as its corresponding Swedish acronym) were carried out using a micro-pyrolyzer equipped with gas chromatography-mass spectrometry/flame ionization detector (Pyro-GC/MS) to investigate the catalytic performance of the developed catalysts and a commercial HZSM-5 catalyst on the selectivity of BJF chemical compounds produced from pyrolysis and catalytic pyrolysis of sawdust and grot (WP2). Meanwhile, the ultra-thin defect-free ZSM-5 catalyst was tested in the packed-bed reactor at LTU to convert ethylene, a mixture of ethylene and benzene, and a biomass pyrolysis oil model consisted of guaiacol, syringol, methanol and water into bio jet fuels (BJFs). The experimental upgrading of model bio-oils was performed in a fixed bed reactor of 6 mm in diameter and a length of 140 mm (WP3).

A bench-scale ex-situ catalytic fast pyrolysis system (continuous drop tube pyrolyzer) available at RISE was used for conversion of sawdust into BJF components (WP4). The effect of pyrolysis and catalyst bed temperatures, catalyst loading, residence time, pyrolysis atmosphere, etc. on the yield and composition of the upgraded bio-oil was investigated. As process improvement, effect of different pyrolysis atmospheres, such as N_2, H_2/N_2, and air/N_2, on the selectivity of bio jet fuel components was studied. In addition, the reusability of developed catalysts was studied for four times recycling/reapplication of the catalysts in sawdust hydropyrolysis process. The fate of oxygenated compounds (e.g. volatile acids/aldehydes/ketones) that cause corrosivity and instability in the oils and over-converted products (e.g. substituted naphthalenes) was investigated. In WP4, a mixture of two home-made catalysts, HRCHY HBeta and Mo/TiO_2 as respectively cracking and hydroconversion catalysts, were used for direct conversion of sawdust into BJF components via ex-situ catalytic hydropyrolysis process.

In addition to this final report to the Swedish Energy Agency, the experimental data achieved in this project were presented in national and international workshop and conferences and were compiled as scientific manuscripts for publication in peer-reviewed scientific journals (WP5 and WP6).

Results

Micro-scale analytical pyrolysis of sawdust and grot using the home-made catalysts of ultra-thin defect-free ZSM-5 (ZSM-5-F) and the hierarchical HBeta (HRCHY HBeta) as well as the commercial catalyst of HZSM-5 showed that both the home-made catalysts were as active as the commercial HZSM-5 to convert the pyrolysis vapors from sawdust and grot into aromatic BJFs. The ZSM-5-F was a selective catalyst for conversion of pyrolyzates of sawdust and grot into BTX (benzene, toluene, and xylenes) and monoaromatic HCs. Catalyst configuration (in-situ or ex-situ) had no effect on the selectivity of BTX in the pyrolysis of sawdust and grot using the developed zeolite catalysts of ZSM-5-F and HRCHY HBeta. Type of biomass feedstock affected the synergy between the catalysts of different structures in the formation of BTX. For instance, in contrast to sawdust, the mixture of catalysts showed synergy in the formation of BTX via in-situ catalytic pyrolysis of grot.

A mixture of ethylene and benzene was processed in the packed-bed reactor at LTU using the ZSM-5-F catalyst, and the results showed that the catalyst was deactivated rapidly. However, feeding only ethylene into the packed-bed reactor resulted in a high formation of BJF chemicals together with a long stability of the catalyst. The catalyst could actively (constant 100% ethylene conversion and up to constant 82% selectivity to jet fuel chemicals) work for a long time (four days operation time). This catalyst was also tested for the conversion of bio-oil model compounds consisting of syringol, guaiacol, methanol, and water into BJFs. However, the bio-oil models caused rapid deactivation of the synthesized ZSM-5-F catalyst. Since this catalyst was deactivated rapidly while converting phenolic compounds of bio-oil, as the most dominant pyrolysis intermediates, this project did not investigate the application of this catalyst for direct conversion of real biomass (sawdust in this project) into BJFs using the ex-situ catalytic fast pyrolysis system at RISE.

However, as planned, the HRCHY HBeta prepared at RISE was used in the conversion of sawdust biomass into BJFs using the bench-scale continuous pyrolyzer at RISE. The reaction conditions were optimized for a higher selectivity of BJF components in the downstream bio-oil product. A combination of the HRCHY HBeta, as cracking catalyst, with Mo/TiO_2, as hydroconversion catalyst, was used in the fixed bed catalytic reactor attached to the pyrolzer in ex-situ configuration. The catalyst design used in this project for catalytic hydropyrolysis of sawdust into BJFs improved the diffusion rate of reactants/products to and from the catalyst active sites, enhancing the selectivity towards aromatic hydrocarbons in the range of jet fuels. Compared to the selectivity towards BJFs while only Mo/TiO_2 was used, the formation of BJFs increased considerably (for about two times) while combining HRCHY HBeta with Mo/TiO_2 catalyst. The developed HRCHY HBeta was compared with the commercial HBeta as cracking catalyst and the results showed that the performance of HRCHY HBeta in the formation of BJFs was better with 1.4 times higher selectivity towards BJFs. Two different catalyst bed temperatures of 350 °C and 400 °C were tested while higher selectivity to BJF components was observed at 400 °C. Carbonyl contents of the bio-oils produced via thermal pyrolysis (without catalyst) and catalytic hydropyrolysis were measured to evaluate the stability character of bio-oils considering that lower carbonyls mean higher stability of bio-oils. Catalytic hydropyrolysis of sawdust using HRCHY HBeta and Mo/TiO_2 catalysts considerably reduced the carbonyl contents for 51% compared to the thermal pyrolysis of sawdust in which no catalyst was used. The ratio of HRCHY HBeta to Mo/TiO_2 catalyst was optimized since the experimental results showed that this parameter considerably affected the selectivity to BJFs. Maximum selectivity to BJFs (42 FID area%) was observed when the content of HRCHY HBeta was 17% in total amount of catalyst used.

This study investigated the importance of having a harmony between catalyst properties, reaction conditions, and chemical reactions of interest in direct conversion of sawdust into BJF components via pyrolysis process. Hence, a bed of catalyst consisting of HRCHY HBeta followed by Mo/TiO_2 was built and used for upgrading the sawdust pyrolysis vapors into BJFs. The catalytic fast pyrolysis process employed in this study improved the diffusion rate of reactants/products to and from the catalyst active sites, enhancing the selectivity towards aromatic hydrocarbons in the range of jet fuels. The key factor was to allow the sawdust pyrolysis vapors to be cracked further over a well-designed micro- and mesopore cracking catalyst (HRCHY HBeta) and then be hydrotreated over an efficient hydroconversion catalyst (Mo/TiO_2). In this concept, the HRCHY HBeta with suitable pore sizes and acidity could improve the performance of Mo/TiO_2 in BJF production. The results of this research demonstrated that catalytic hydropyrolysis of sawdust using the mixed catalysts in ex-situ configuration was an effective method for selective production of BJF components. Catalytic hydropyrolysis significantly eliminated the aliphatic alcohols/ethers/carbohydrates and carboxylic acids/esters, while improved the aromatics/alkenes of bio-oil, enhancing the quality of carbon-containing components and HHV of liquid product.

The lifetime of catalysts was investigated while the catalysts were regenerated and reused in hydropyrolysis of sawdust for several times. Specifically, the durability of catalysts was evaluated for four times and the results showed that the catalysts combination resulted in similar selectivity to BJFs during recycling tests. The catalysts were still actively catalysing deoxygenation reactions during the 4th catalyst reusability test. In comparison to the bio-oil obtained after the 1st catalytic hydropyrolysis test, the high heating value (HHV) and deoxygenation degree (DDO) of bio-oil obtained after the 4th recycling test were slightly reduced for 2.9% and 6.9%, respectively. Selectivity to BJF components in bio-oil remained constant after regeneration and reapplication of the catalysts for hydropyrolysis tests. Meanwhile, the SEM images of fresh and spent catalysts showed that the structure of catalyst did not change after four times recycling tests. The N_2 adsorption-desorption analysis of fresh and spent catalysts showed that the surface area and total pore volume of the catalysts changed slightly indicating that the developed catalysts could keep their properties even after four times regeneration processes and recycling tests.

The effect of pyrolysis gas atmospheres of N_2 (catalytic pyrolysis), H_2/N_2 (catalytic hydropyrolysis), and air/N_2 (catalytic oxidative pyrolysis) on the selectivity of BJF components in the bio-oil products was investigated. Experimental results showed that the DDO of the pyrolysis intermediates was considerably low and consequently the selectivity to BJF was very low while H_2 was removed from the pyrolysis carrier gas composition. The efficiency of different pyrolysis processes (thermal pyrolysis, catalytic pyrolysis, catalytic hydropyrolysis, and catalytic oxidative pyrolysis) in carbon recovery was investigated and it was observed that compared to thermal pyrolysis the total carbon recovery in catalytic hydropyrolysis was reduced and the concentration of carbon compounds in pyrolysis gas was significantly increased while that in pyrolysis liquid was considerably reduced. In oxidative pyrolysis, the total carbon recovery was improved than the thermal pyrolysis while a significant increase in the carbon compounds of solid and gas products was observed. In total, the maximum carbon recovery was achieved in catalytic pyrolysis process. There, a significant increase in the carbon compounds of solid product, a lower reduction in the concentration of carbon compounds in bio-oil, and an increased concentration of carbon compounds in pyrolysis gas were achieved. Therefore, it is inferred that hydrogen is a key element in the direct conversion of biomass in general and sawdust in particular into BJF via pyrolysis process while a suitable catalyst is employed. Production of a higher quality of pyrolysis liquid was accompanied with about 8 wt% carbon loss in catalytic hydropyrolysis of sawdust than the thermal pyrolysis. The generation of BJFs in the pyrolysis liquid produced via catalytic hydropyrolysis was significantly improved compared to thermal pyrolysis, catalytic pyrolysis, and catalytic oxidative pyrolysis at the cost of sacrificing carbon efficiency of the process. Without hydrogen, the deoxygenation degree was considerably low; DDO was 58% in catalytic hydropyrolysis compared to 19% in catalytic oxidative pyrolysis and 20% in catalytic pyrolysis. The results showed that catalytic hydropyrolysis could be a feasible way to process sawdust into aviation fuels with six- and five-times higher effectiveness compared to catalytic pyrolysis and catalytic oxidative pyrolysis, respectively.

The project concept and data were presented at international conferences of *7th Green & Sustainable Chemistry Conference* and *Nordic Wood Biorefinery Conference (NWBC)* as well as at a *workshop organized by Swedish Energy Agency via Bio+ program*. One article prepared using the experimental data of the tests related to Pyro-GC/MS and fixed bed catalytic conversion of bio-oil model has been accepted for publication in the journal of *Catalysis Letters*. Another article is under preparation using the experimental data achieved from the pyrolysis of sawdust in the continuous drop tube pyrolyzer.

Discussions

In analytical pyrolysis of sawdust and grot, production of BJF HCs using catalysts combination differed in both in-situ and ex-situ catalytic pyrolysis models with respective HCs productions using either of the catalysts as standalone in either of the in-situ and ex-situ conditions. Some combination of catalysts slightly changed the formation of BJF aromatics in both in-situ and ex-situ configurations compared to the catalysts' standalone styles. This effect was dependent to the feedstock type. When the experimental results, while mixing two different catalysts, are as expected from the theoretical calculations (using data obtained from the tests performed using the standalone catalysts), it means that each catalyst behaves according to its specific character with no influence from the other one. However, having synergy on the production of specific compounds like monoaromatic HCs shows that the catalysts mixed are helping each other on proceeding the reactions to that specific chemical product. Having a synergy for the combination of ZSM-5-F with HBeta and HRCHY HBeta in the in-situ catalytic pyrolysis of sawdust could be due to the higher acidity of HBeta and HRCHY HBeta improving the immediate degradation of the sawdust pyrolyzates. Besides, presence of mesopores channels in HBeta and HRCHY HBeta could reduce the diffusion length and accelerate the diffusion rate of larger pyrolysis intermediates and result in distinctive enhancement of mass transport. More degradation of pyrolyzates provides intermediates with smaller sizes which could be more suitable for the channel structure of ZSM-5-F facilitating the upgrading reactions. In addition, higher porosity of HBeta and HRCHY HBeta could help the degradation of sawdust pyrolyzates in in-situ configuration since probably by increasing the immediate penetration of pyrolysis vapors into the catalyst pores. It can be inferred that for sawdust and in in-situ configuration both higher acidity and porosity features of the catalysts helped each other to proceed the reaction towards the target products of BJF HCs. On the other hand, in the in-situ catalytic pyrolysis of grot, the ZSM-5-F only showed synergy with HBeta, and the HBeta showed synergy with both ZSM-5-F and HRCHY HBeta. The reason that HRCHY HBeta and ZSM-5-F could not facilitate the formation of BJF HCs in a 50/50 w/w combination could be due to the size of the pyrolysis intermediates leaving the pores of HRCHY HBeta which could be still large for the channel sizes of ZSM-5-F acting as inhibitor to the target reaction mechanisms. On the contrary, lower acidity and pore size of the HBeta seems suitable to produce pyrolysis intermediates that can be further upgraded by ZSM-5-F. This different behaviour of ZSM-5-F while using different feedstocks of sawdust and grot can be due to the different distribution of their key chemical components of cellulose, hemicellulose, and lignin. The grot has higher lignin and lower cellulose, and hemicellulose contents compared to the sawdust. Lignin has a more complex structure compared to cellulose and hemicellulose which causes the formation of large pyrolysis intermediates which has high polymerization tendency. In fact, degradation of cellulose and hemicellulose is mainly acid-catalyzed reaction. Although the mixture of catalysts showed no synergy in the ex-situ catalytic pyrolysis of sawdust, in the case of grot as feedstock similar catalytic synergy trend was observed in the ex-situ catalytic pyrolysis as was in the in-situ configuration. This reveals the importance of having optimum acidity and porosity in catalyst for pyrolysis of lignin fraction of biomass via both in-situ and ex-situ catalytic pyrolysis.

Practically, catalytic hydropyrolysis of biomass with suitable configuration of efficient catalysts may lead to high yield of BJF components in bio-oil. Selection of suitable catalyst is critical as it significantly influences the distribution and quality of pyrolysis products (oil, char and gas). Catalysts used for upgrading of pyrolysis vapors/oil are rapidly deactivated due to deposition of coke generated over their active sites blocking the catalyst channels and pores. Coke could also be formed due to trapping and polymerization of chemical compounds inside the catalyst channels and pores. Mechanistically, the long chain organic compounds in the biomass pyrolysis vapors can be trapped inside the catalyst pores clogging the catalytic active sites and making them unavailable for further reactions. Therefore, the catalyst used for instance for directly upgrading biomass pyrolysis vapors in a hydrogen rich atmosphere needs to be designed considering the properties of pyrolysis vapors and the properties of products after the upgrading process. Thus, the procedure used to design the chemical and physical structure of a catalyst is important for each individual chemical reaction. An efficient catalyst for biomass hydropyrolysis process requires (i) an improved diffusion rate of reactants/products to and from the catalyst active sites, (ii) suppression of secondary reactions, and (iii) prevention of deactivation mechanisms. These features prevent the fast deactivation of catalyst due to process disharmonious concerning reactants and catalyst properties. Technically, the intermediates of biomass pyrolysis are still big for the pores and channels of many hydrotreatment catalysts which can cause fast deactivation of the catalyst. Therefore, in catalytic hydropyrolysis of biomass, multifunctional catalysts catalysing cracking and hydrotreating reactions are needed while the long chain organic compounds of biomass pyrolysis first are converted into smaller molecules and then those smaller molecules are transformed into target products, such as jet fuel components, via hydrotreating reactions. According to the results of this project, a structure modified zeolite catalyst together with a suitable hydrotreatment catalyst improved the selectivity of sawdust pyrolysis products to BJF components.

Publications list

- Structure-modified zeolites for an enhanced production of bio jet fuel components via catalytic pyrolysis of forestry residues, Waqar Butt, Judith Hernandez Cabello, Jonas Hedlund, Hoda Shafaghat, Accepted for publication in the journal of ***Catalysis Letters.***
- Manuscript title: Direct conversion of sawdust into biobased aviation fuel components via atmospheric catalytic hydropyrolysis process, Submitted to the journal of ***Green Chemistry***.

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Appendix

Appendix A:

Administrativ bilaga.

Appendix B:

Scientific manuscript under preparation:

- Direct conversion of sawdust into biobased aviation fuel components via atmospheric catalytic hydropyrolysis process. Submitted to the journal of *Green Chemistry*.

Appendix C:

Presentations at scientific conferences

- Structure-modified ZSM-5 zeolite for a selective production of BTX in catalytic pyrolysis of biomass, oral presentation, Hoda Shafaghat, 7th Green & Sustainable Chemistry Conference, May 22-24, 2023, Dresden, Germany.
- From forest to low GHG jet biofuels by a developed catalytic fast pyrolysis technology, oral presentation, Hoda Shafaghat, Nordic Wood Biorefinery Conference (NWBC) 15-17, 2024, Örnsköldsvik, Sweden.