

Upgrading Bio-Fuel from Jatropha Oil via One-pot Transesterification-Isomerisation Using Solid Acid Catalysts

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Abstract. This study used transesterification-isomerisation processes to synthesise biodiesel from non-edible vegetable oils, specifically jatropha oil and palm fatty acid distillate (PFAD). To facilitate the separation of products, both were conducted in a batch reactor with a solid acid catalyst. Additionally, a one-pot isomerisation reaction was carried out to improve the cold flow properties of the biodiesel by reducing its cloud point. The skeletal isomerisation results showed a significant variation in the conversion rate of methyl oleate, ranging from 0% to 100% at 250°C, depending on the catalyst used. Al-SBA-15 achieved a 100% conversion rate at 250°C, significantly reducing the biodiesel cloud point. The esterification reaction results indicated that the conversion rate of fatty acids was 100% at 150°C when either MPS (sulfonic SBA-15) or Al-SBA-15 catalysts were used. Moreover, by increasing the skeletal isomer product, the viscosity and melting point of upgraded bio-oil can be decreased.

1. Introduction

Biodiesel has gained significant attention in recent years as a viable alternative to fossil fuels due to its renewable nature and lower environmental impact [1-3]. It is typically produced from various feedstocks, including vegetable oils, animal fats, and waste cooking oils. The primary production processes, catalytic esterification and transesterification, involve converting these feedstocks into fatty acid methyl esters (FAME), the main component of biodiesel. These processes are widely adopted for their operational simplicity and economic feasibility.

Transesterification, the more commonly used method, involves the reaction of triglycerides with alcohol in the presence of a base catalyst, producing biodiesel and glycerol as a by-product [4, 5]. Although effective, this method requires additional steps for catalyst

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separation, which can complicate the production. Recent developments in solid catalysts have simplified this process, enhancing efficiency and reducing production costs. For feedstocks with high free fatty acid content, esterification is often employed. Both methods are instrumental in large-scale biodiesel production and contribute to the reduction of greenhouse gas emissions, making biodiesel an attractive alternative to conventional petroleum-based fuels [6].

However, despite these advancements, challenges persist with the use of homogeneous catalysts. These catalysts are difficult to recycle, generate large volumes of wastewater, and are not suitable for feedstocks with high free fatty acid content, as they may cause undesirable side reactions. Additionally, homogeneous acid catalysts, while more compatible with such feedstocks, present issues such as slow reaction rates, equipment corrosion, and the need for complex purification steps [7].

To address these drawbacks, heterogeneous catalysts, particularly solid acid catalysts, have been explored as a more efficient and sustainable alternative. These catalysts offer the advantages of recyclability, reduced wastewater production, and simplified separation processes. Solid acid catalysts are especially promising for feedstocks with high free fatty acid content, and their use has the potential to significantly improve the efficiency of biodiesel production [8].

Although significant progress has been made with heterogeneous catalysts, the quality of biodiesel still faces several limitations, including poor cold flow properties, high cloud points, and low heating values, particularly under low-temperature conditions. One promising solution to these issues is hydro-isomerisation [9], which modifies the molecular structure of biodiesel to improve its cold flow properties. However, this process is often cost-prohibitive due to the need for hydrogen.

While advancements have been made in biodiesel production, few studies have successfully integrated transesterification and isomerisation processes into a single step using solid acid catalysts, especially for feedstocks like *Jatropha* oil. This study aims to develop a heterogeneous solid acid catalyst that is capable of performing transesterification or esterification while simultaneously facilitating partial isomerisation of biodiesel components in a single-step process. By integrating isomerisation within the production process, this approach seeks to improve the cold flow properties of biodiesel without the high costs associated with hydrogen-based hydro-isomerisation. The proposed method has the potential to offer a more efficient, cost-effective, and sustainable solution for producing high-quality biodiesel from non-edible vegetable oils (*Jatropha* oil).

2. Methodology

2.1 Catalysts preparations and characterisation

Al-SBA-15:

The direct synthesis method of Al-SBA-15 used 10.63 g of TEOS, 3.23 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Si/Al=10 or 5), 5 g of P123, 150 g of 2M HCl, and 37.5 g of water. After mixing and stirring at 40°C, the solution underwent hydrothermal treatment at 100°C for 2 days, followed by filtering, drying, and calcining at 550°C for 6 hours.

5wt% Zr-SBA-15/SO₄²⁻:

This catalyst was prepared via impregnation. A mixture of 200 ml ethanol and 1.81 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was heated at 60°C, and then 9.5 g SBA-15 was added. The ethanol was evaporated, and the solid was dried at 80°C, then calcined at 600°C for 10 hours. The solid was treated with 1M H₂SO₄, followed by drying and calcining at 650°C for 3 hours.

ZrO₂/SO₄²⁻:

30 g of RSC-HP was pulverised, treated with 1M H₂SO₄ for 1 hour, filtered, dried at 60°C for 18 hours, and calcined at 650°C for 3 hours.

10wt% Nb₂O₅-SiO₂:

Solution A was prepared by mixing 24.74 g TEOS, 50 ml ethanol, and 0.86 ml HCl and stirred at 80°C for 2.5 hours. Solution B, containing 1.52 g NbCl₅ and 100 ml ethanol, was mixed under N₂ atmosphere and combined with solution A for 3 hours. The mixture was stirred with water for gel formation, followed by drying at 110°C and calcination at 800°C.

MPSD (Mesoporous Silica):

12 g of P123 was dissolved in 375 g of 2M HCl, followed by the addition of 28.77 g of TEOS for hydrolysis. 6.78 g of 3-mercaptopropyl trimethoxysilane was added, followed by oxidation with H₂O₂. The mixture was stirred at 40°C for 20 hours, aged at 90°C for 36 hours, filtered, and washed using a Soxhlet extractor with ethanol. The final product was vacuum dried at 65°C.

All prepared catalysts were characterised through several analyses. BET analysis was conducted using a Belsorp-mini II device (Bel Japan) to measure surface area. Acidity tests were carried out using FTIR pyridine adsorption and titration methods.

2.2 Activity tests and its analysis

To evaluate the catalytic activity of the catalysts, three different compounds were used. First, a model compound, methyl oleate, was employed to investigate isomerization reactions. Additionally, bio-oil from *Jatropha* oil and palm fatty acid distillate (PFAD) was used for esterification and transesterification experiments.

The activity tests for solid acid catalysts in esterification and transesterification were conducted using a batch reactor (AC-120). The catalysts were dried at 120°C for 30 minutes before use. The esterification reaction was carried out for 6 hours at varying temperatures between 100°C and 200°C, using a molar ratio of PFAD to methanol of 6:1, with the catalyst amount set to 10 wt% of the oil. For the transesterification reaction, conditions were set for 6 hours with temperatures ranging from 200°C to 300°C. The mass ratio of *Jatropha* oil, methanol, and catalyst was set at 5:17:1. At lower temperatures, a molar ratio of 1:6 (*Jatropha* oil to methanol) was used, with the catalyst amount at 10 wt% of the oil. The set temperature and reaction conditions were based on the optimal parameters required to achieve a maximum conversion of 100%.

Once all materials were added to the reactor, nitrogen was used to purge the reactor to eliminate oxygen. After the reaction was completed, the product and catalyst were separated via centrifugal separation. For reactions involving methanol, water was added to the mixture to remove any residual methanol. After separating the product and water, the washed product was heated at 120°C for 1 hour to evaporate the remaining water.

The products were analysed using GC-FID 2025 (SHIMADZU) and GC-FID 14B (SHIMADZU). Melting point measurements were conducted using an electric thermometer with the following steps: The sample bottle was first frozen by placing it in a methanol bath at -50°C. Once the sample reached -30°C, the bottle was allowed to warm to room temperature. The melting point was recorded as the temperature at which the sample began to melt. The viscosity of the products was also measured using rotational viscometers.

3. Results and discussion

3.1 Characterisations of catalysts

The surface area of the prepared catalysts was measured using BET methods, as presented in Table 1. SBA-15 and MPSD are mesoporous silica materials with higher surface areas compared to other catalysts. In the case of Al-SBA-15, an increase in aluminium content leads to a decrease in surface area, from 784 m²/g to 434 m²/g when the Si/Al ratio is 10 and 5, respectively. Zirconia-doped SBA-15 also shows a lower surface area compared to Al-SBA-15. The average pore size of the prepared catalysts ranges from 2-6 nm, with ZrO₂/SO₄ having the largest pore size at approximately 15.9 nm

Table 1. Specific surface area and pore size of prepared catalysts

Catalysts	BET analysis results		
	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	d _{avg} (nm)
Al-SBA 15(10)	784	0.89	4.5
Al-SBA 15(5)	434	0.64	5.9
5wt%Zr-SBA-15/SO ₄	595	0.68	3.9
MPSD	698	0.66	3.7
10wt%Nb ₂ O ₅ / SiO ₂	277	0.20	2.4
ZrO ₂ /SO ₄	33	0.14	15.9

The acidity content of the prepared catalysts was measured using titration and FTIR pyridine adsorption. The results from the titration method used to calculate the acidity of each catalyst, are presented in Table 2. The highest acidity was observed in MPSD, with Al-SBA-15 in second place. By increasing the aluminium content, the acidity of Al-SBA-15 increased from 0.6 mmol/g for Al-SBA-15(10) to 1.36 mmol/g for Al-SBA-15(5).

Table 2. Acidity amount of solid acid catalysts by titration methods

Catalysts	M (g)	V NaOH (ml)	Acid amount (mmol/g)
Al-SBA-15(10)	0.1080	0.65	0.6
Al-SBA-15(5)	0.1101	1.50	1.36
5wt%Zr-SBA15/SO ₄	0.1016	1.10	1.08
ZrO ₂ /SO ₄	0.1085	0.30	0.28
MPSD	0.1004	1.5	1.49
5wt%Nb ₂ O ₅ / SO ₄	0.1000	0.50	0.50

To further assess the Bronsted acid and Lewis acid of the doping SBA-15, FTIR-pyridine was performed at different temperatures (100, 200 and 300°C) and the results are presented in Table 3 and Figure 1. Zr/SBA-15/SO₄ showed a higher concentration of Lewis acid but not Bronsted acid. In contrast, Al-SBA-15 contain both Bronsted acid and Lewis acid. Both catalysts exhibit medium and weak acidity, as indicated by prominent peaks at lower temperatures.

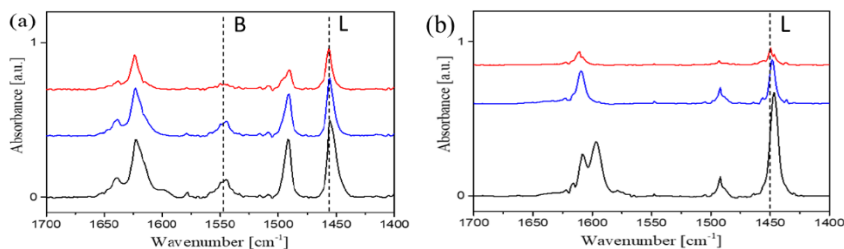


Fig. 1. The pyridine-adsorption FTIR spectra of (a)Al-SBA-15(5) and (b)5%Zr/SBA-15/SO₄.

Table 3. Bronsted and Lewis acid amount of Al-SBA-15 and Zr/SBA-15/SO₄.

Catalysts	Acid Type	Acid site concentration		
		100°C	200°C	300°C
Al-SBA-15(10)	L	131	78	53
	B	59	41	17
Al-SBA-15(5)	L	132	76	64
	B	57	51	56
5%Zr-SBA-15/SO ₄	L	129	40	17
10%Zr-SBA-15/SO ₄	L	110	115	106

3.2 Isomerisation of methyl oleate

An activity test of the various catalysts was conducted using methyl oleate as a model compound to evaluate the ability of different solid acid catalysts to perform skeletal isomerisation reactions. Table 4 summarises the conversion of methyl oleate at 200°C for 6 hours.

Table 4. Conversion of methyl oleate in isomerisation using different solid acid catalysts.

Catalysts	Acid type	Reaction Condition	Conversion of methyl oleate
Al-SBA 15(5)	B	200°C, 6h	42.5%
ZrO ₂ .SO ₄	L	200°C, 6h	22.7%
Nb ₂ O ₅ .SiO ₂	L	200°C, 6h	1.0%
Zr-SBA15- SO ₄	L	200°C, 6h	4.5%
HZSM 22	B	200°C, 6h	0.0%

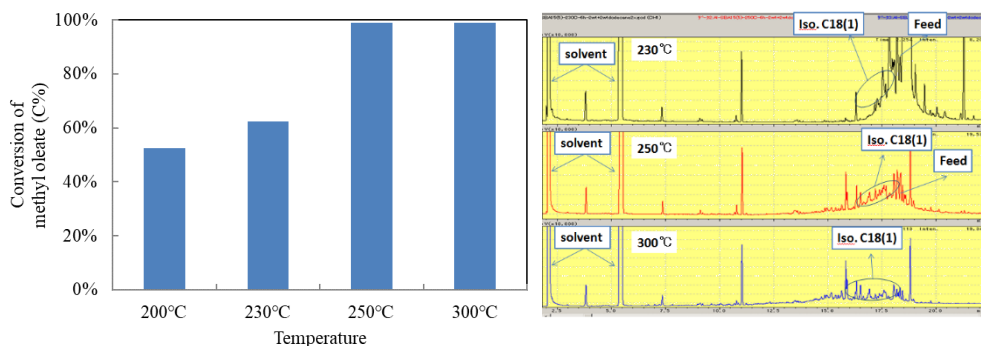


Fig. 2. Conversion of methyl oleate using Al-SBA-15 and its GC pattern at different temperature.

Al-SBA-15 achieved the highest conversion rate of methyl oleate at 42.5%. The high conversion rate may be attributed to the increased content of Brønsted acid, as confirmed by other studies showing that Brønsted acid can accelerate isomerisation reactions [10]. To achieve the highest conversion, the effect of temperature was investigated, and Al-SBA-15 was selected for testing due to its superior selectivity towards the isomerisation reaction. The effect of temperature is presented in Figure 2, which shows that Al-SBA-15 achieved a 100% conversion of methyl oleate at a relatively low temperature of 250°C.

3.3 Esterification and transesterification of bio-oil

After confirming the skeletal isomerisation reaction using various types of solid acid catalysts, as explained in the previous section, the best-performing catalyst was tested with real bio-oils (Jatropha oil and palm fatty acid distillate (PFAD)) for transesterification and esterification reactions. Using PFAD as the material for the esterification reaction, 100% conversion was achieved with Al-SBA-15(5) and MPSD, both of which have high surface areas and acidity. The composition of the upgraded bio-oil is presented in Figure 3. The selectivity for the isomerisation product was 40% with Al-SBA-15(5) and around 18% with 5 wt% Zr-SBA15/SO₄. The higher isomerisation rate observed with Al-SBA-15 is attributed to its higher concentration of Brønsted acid, as outlined in Table 3.

Table 5. Esterification reaction of PFAD with different catalysts and temperature

Catalysts	Reaction condition	Conversion of fatty acid (C%)	Yield of FAME (C%)			
			C16:0	C18:0	C18:1	C18:2
Al-SBA15(10)	150°C, 6h	94.81	38.28	1.46	47.74	8.87
5wt% Zr-SBA15/SO ₄	150°C, 6h	92.78	40.32	1.06	44.17	7.23
Al-SBA15(5)	150°C, 6h	100	39.8	8.1	43.3	8.9
Al-SBA15(5)	130°C, 6h	80.3	36.8	0.5	35.8	7.2
Al-SBA15(5)	100°C, 6h	55.6	25.5	0.4	24.8	4.9

MPSD	150°C, 6h	100	45.0	1.5	45.1	8.5
MPSD	100°C, 6h	98.9	45.3	0.8	44.1	8.7
5wt% Zr-SBA15/SO ₄	150°C, 6h	92.78	40.32	1.06	44.17	7.23

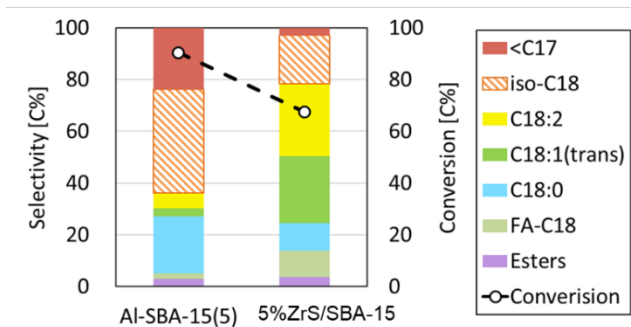


Fig. 3. Composition of bio-oil from esterification product of PFAD.

In the case of *Jatropha* oil, the conversion rate of triglycerides using Al-SBA-15(10) reached 100% at 250°C, as shown in Table 6. The selectivity for the isomerisation compound was only 9.4%, as presented in Figure 4. Once again, Al-SBA-15(10) demonstrated superior performance in the isomerisation reaction compared to ZrS/SBA-15.

Table 6. Transesterification of *Jatropha* oil at different temperature.

Catalysts	Reaction condition	Conversion of triglyceride (C%)
Al-SBA15(10)	150°C, 6h	47%
Al-SBA15(10)	200°C, 6h	83%
Al-SBA15(10)	250°C, 6h	100%
Al-SBA15(10)	300°C, 6h	100%

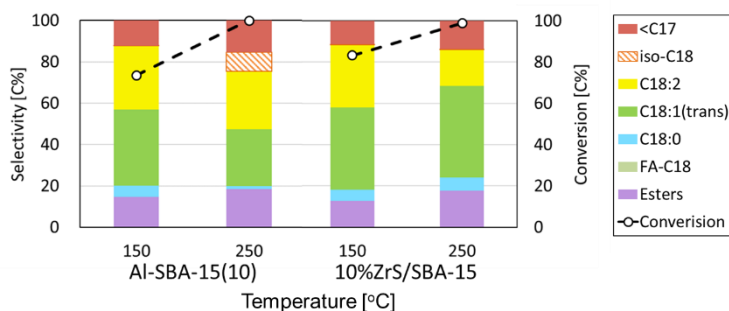


Fig. 4. Bio-oil composition from transesterification product of *Jatropha* oil.

3.4 Upgraded bio-oil characterisation

The upgraded bio-oil produced through esterification was then tested to measure the melting point, with the results presented in **Table 7**. It is evident that the one-pot esterification-isomerisation reaction of methyl oleate (MO) and PFAD reduced the melting point by approximately 20°C and 40°C, respectively. Additionally, the viscosity of the upgraded oil decreased compared to the raw Jatropha oil as depicted in **Figure 5**.

Table 7. Melting point measurement of esterification and isomerisation product of MO and PFAD

Materials (Catalysts)	Reaction condition	Conversion (C%)	MP (°C)
Methyl Oleate (MO)			10
MO isomerisation (Al-SBA15 (5))	300°C, 6h	99.7%	-12
MO isomerization (SiO ₂ .10wt%Nb ₂ O ₅)	300°C, 6h	79.2%	-8
Palm Fatty Acid Distillate (raw material)			50
PFAD esterification (Al-SBA-15(5))	150°C, 6h	100%	8
PFAD esterification (MPS)	150°C, 6h	100%	10
PFAD esterification (Zr-SBA-15/SO ₄)	150°C, 6h	92.7%	20

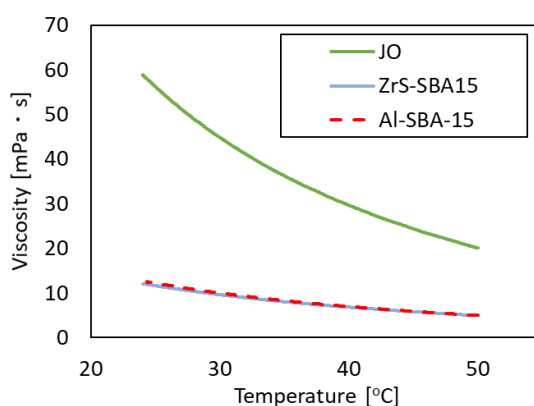


Fig. 5. Viscosity measurement for upgraded bio-oil from Jatropha oil.

Al-SBA-15 achieved the highest conversion rate of 100% for both transesterification and isomerization, likely due to its higher Brønsted acidity and favourable mesoporous structure. This structure allows for better diffusion of reactants, leading to improved catalytic activity compared to catalysts like ZrO₂/SO₄, which had a lower surface area and acidity. The higher acidity in Al-SBA-15 enables faster proton donation, which is crucial for esterification and isomerisation reactions, thereby enhancing the efficiency of biodiesel production. Additionally, Al-SBA-15 exhibits ultra-stable mesopores and a high Brønsted acid content, as shown in other studies [11, 12].

The successful integration of transesterification and isomerization using solid acid catalysts like Al-SBA-15 has the potential to streamline biodiesel production by combining two critical steps into one. This could lead to reduced processing times and operational costs in industrial settings, making biodiesel production more economically feasible. Future work could focus on optimizing this one-pot process for various feedstocks to further increase its industrial applicability.

References

1. C. Sanjurjo, P. Oulego, M. Bartolomé, E. Rodríguez, R. Gonzalez, and A. Hernández Battez, Biodiesel production from the microalgae *Nannochloropsis gaditana*: Optimization of the transesterification reaction and physicochemical characterization. *Biomass and Bioenergy*. **185**, 107240 (2024). <https://doi.org/10.1016/j.biombioe.2024.107240>.
2. I. Purnama, W. Trisunaryanti, K. Wijaya, A. Mutamima, W. C. Oh, R. Boukherroub, & M. Aziz. Multi-Pathways for Sustainable Fuel Production from Biomass Using Zirconium-Based Catalysts: A Comprehensive Review. *Energy Technology*. **12**(2), 2300901 (2024).
3. T. Yao, H. T. K. Nguyen, A. Mutamima, T. Maki, Y. Guo, M. Sakurai, & H. Kameyama. Steam reforming of ethanol over electrically-heated anodic aluminum catalysts for hydrogen production. *International Journal of Hydrogen Energy*. **40**(35), 11863-11871 (2015).
4. M. Salaheldeen, A. A. Mariod, M. K. Aroua, S. M. A. Rahman, M. E. M. Soudagar, and I. M. R. Fattah, Current State and Perspectives on Transesterification of Triglycerides for Biodiesel Production. *Catalysts*. **11**, 1121 (2021). <https://www.mdpi.com/2073-4344/11/9/1121>.
5. K. S.H. Eldiehy, P. Bardhan, D. Borah, M. Gohain, M. A. Rather, D. Deka, M. Mandal, A comprehensive review on microalgal biomass production and processing for biodiesel production. *Fuel*. **324**, 124773 (2022). doi: 10.1016/j.fuel.2022.124773.
6. H. Mohamadzadeh Shirazi, J. Karimi-Sabet, and C. Ghotbi, Biodiesel production from *Spirulina* microalgae feedstock using direct transesterification near supercritical methanol condition. *Bioresource Technology*. **239**, 378-386 (2017). doi: 10.1016/j.biortech.2017.04.073.
7. J. Lilja, D. Y. Murzin, T. Salmi, J. Aumo, P. Mäki-Arvela, and M. Sundell, Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation. *Journal of Molecular Catalysis A: Chemical*. **182-183**, 555-563 (2002). [https://doi.org/10.1016/S1381-1169\(01\)00495-2](https://doi.org/10.1016/S1381-1169(01)00495-2).
8. R. M. Thomas, M. S. L. Lemus, K. Ganesh, D. B. Obbard, K. Sivashanmugam, G. Sambasivam, Y. Yang and B. H. Lipshutz, Dehydration in water: solid-supported lipases as green catalysts for esterification. *Green Chemistry*. **26**, 9320-9329 (2024) doi: 10.1039/D4GC02904F.
9. M. L. Gunawan, T. H. Novita, F. Aprialdi, D. Aulia, A. S.F. Nanda, C. B. Rasrendra, Z. Addarajah, D. Mujahidin, G. T.M. Kadja, Palm-oil transformation into green and clean biofuels: Recent advances in the zeolite-based catalytic technologies. *Bioresource Technology Reports*. **23**, 101546 (2023) <https://doi.org/10.1016/j.biteb.2023.101546>.
10. T. K. Dharmapriya, K. Y. A. Lin, and P. J. Huang, Roles of Brønsted-Base and Brønsted-Acid Catalysts for Glucose Isomerization into Fructose and Fructose Dehydration into 5-Hydroxymethylfurfural. *Energy Fuels*. **38**, 16834-16852 (2024) <https://doi.org/10.1021/acs.energyfuels.4c02551>.
11. R. Liu, W. Cai, X. Ni, L. Shi, R. Wang, S. Lin, Ultrastable and strongly acidic Al-SBA-15 with superior activity in LDPE catalytic cracking reaction. *Journal of Solid State Chemistry*. **286**, 121319 (2020) <https://doi.org/10.1016/j.jssc.2020.121319>.
12. A. J.J. Koekkoek, J.A. R. Veen, P. B. Gerritsen, P. Giltay, P. C.M.M. Magusin, E. J.M. Hensen, Brønsted acidity of Al/SBA-15. *Microporous and Mesoporous Materials*. **151**, 34-43 (2012) <https://doi.org/10.1016/j.micromeso.2011.11.019>.