Alexander O’Malley - Syd Andrew Fellowship
‘Multiscale understanding of lignin derivative behaviour in industrial zeolite catalysts’
Closeout report – June 2025

The overarching aim of my Syd Andrew Fellowship has been to gain significant insight into the dynamical behaviour of molecules relevant to the catalytic conversion of lignocellulosic biomass inside industrially established zeolite catalysts, through a range of experimental and theoretical methods. Understanding the adsorption and diffusion behaviours of lignin-derived aromatics within established catalysts is crucial for optimising the catalytic conversion of more sustainable, non-fossil, lignin-based feedstocks into value-added fuels and chemicals using existing infrastructure.

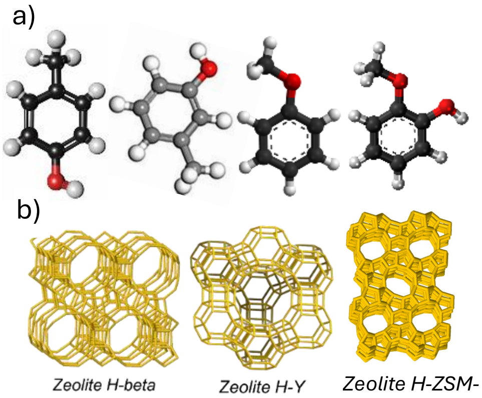

Figure 1. a) (left to right) isomers *p*- and *m*- cresol, anisole and guaiacol. b) (left to right) framework structures of zeolites beta, Y and ZSM-5.

The fellowship focused on a set of key lignin pyrolysis derivatives—anisole (methoxybenzene), guaiacol (2-methoxyphenol), and the *o*-, *m*-, and *p*-cresol isomers (2-, 3-, and 4-methylphenol)— (shown in figure 1a) which collectively account for around 18 wt.% of the products from soda lignin pyrolysis. These molecules are important platform chemicals in the production of fuels and industrially relevant products, including phenols, nylon precursors, agrochemicals, cosmetics, and polymers.

The zeolites studied—H-ZSM-5, H-Beta, and H-Y— are widely used in the chemical industry at scale, and were selected to represent distinct pore systems and include H-Y (13 Å supercages connected by 7 Å windows), H-Beta (intersecting ~6.5 Å channels), and H-ZSM-5 (intersecting straight and sinusoidal 5.5 Å channels) as shown in figure 1b. These differences allowed systematic investigation of how pore shape and size influence molecular mobility and adsorption behaviour.

To gain a comprehensive picture of lignin derivative behaviour, the project integrated complementary experimental and computational methods across multiple length and timescales (Figure 2). At the molecular scale, vibrational spectroscopy and quantum mechanical calculations were used to probe adsorption geometries and acid site interactions. At the nanoscale, quasielastic neutron scattering (QENS) was combined with classical molecular dynamics (MD) to quantify diffusion and rotational behaviours in both bulk and confined systems. The work complements more traditional methods probing longer length scales such as gravimetric sorption measurements and PFG-NMR.

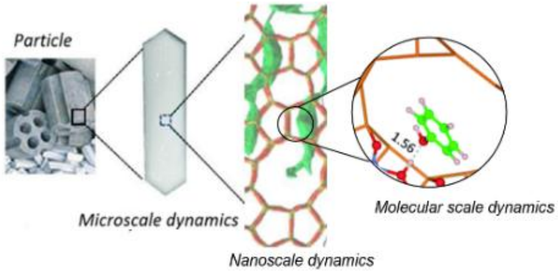

Figure 2. Scales of study on which the Andrew Fellowship project is based.

The specific aims of the fellowship were to:

- Validate classical simulation models for describing the dynamics of lignin-derived aromatics in the liquid state, ensuring reliable force field parameterisation for subsequent studies.
- Quantify the local and nanoscale dynamics of a representative set of lignin pyrolysis monomers in the liquid phase, exploring how specific functional group placement influences these behaviours.
- Probe the impact of confinement within zeolite micropores on local and nanoscale mobility of lignin derivatives, identifying how pore geometry, molecular shape, and zeolite Brønsted acid site interactions govern diffusion mechanisms.
- Understand adsorption strength and geometry of the lignin derivatives using vibrational spectroscopy and DFT-based calculations, linking molecular-scale interactions to nanoscale diffusivity across industrially relevant zeolite frameworks.

The work carried out during the fellowship led to 5 peer reviewed published papers in respected journals in fields of catalysis, physical chemistry, porous materials and sustainability science. The results of each study will be briefly detailed herein.

Benchmarking Molecular Models for Lignin Derivatives in the Liquid State[1]

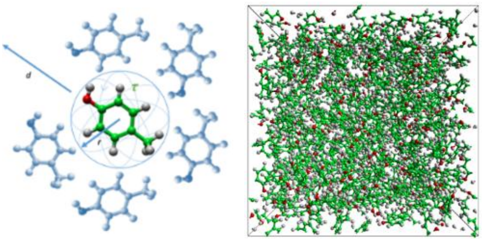

Figure 3. (left) Modes of motion a cresol isomer takes on the nanosecond scale in a liquid, isotropic rotation and jump diffusion. (right) simulation cell of bulk *p*-cresol simulated by classical MD.

Before studying the behaviour of lignin-derived aromatics in the complex environments of zeolite catalysts, it was first essential to establish confidence in the molecular dynamics (MD) simulation methods being used to model their motion on the nanoscale. Classical MD simulations rely on force fields—mathematical models that approximate atomic interactions such as van der Waals forces and hydrogen bonding. The reliability of any diffusion or adsorption predictions hinges on how well these models capture the true dynamical behaviour of the molecules in question.

To this end, the first study focused on the diffusion and rotational dynamics of *p*-cresol in the bulk liquid phase[1], comparing experimental measurements of diffusivity with simulations using two widely adopted force field models: OPLS2005 and OPLS3. *p*-Cresol was selected as a representative system due to its prevalence in lignin pyrolysis oils and its structural simplicity, which makes it a useful benchmark for studying functionalised aromatics.

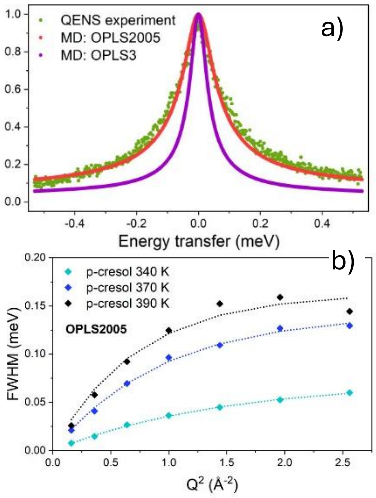

Figure 4. a) Example QENS spectrum of liquid *p*-cresol at 343 K plotted with those generated by classical simulation with different forcefield models. b) QENS line broadenings generated by MD simulations with the best agreeing forcefield model.

Using quasielastic neutron scattering (QENS), both translational jump diffusion and isotropic molecular rotation (figure 3, 4b) were observed across a range of temperatures. These experimental results were then directly compared to molecular dynamics simulations over the same timescales, through reproduction of QENS spectra from the simulation (figure 4a). Both force fields reproduced the overall diffusive behaviour, but differences emerged in the predicted rates of motion. The OPLS3 model, for example, tended to predict slower molecular dynamics, likely due to its increased representation of polarity and stronger hydrogen bonding between cresols, highlighting the sensitivity of lignin-derivative dynamics to subtle differences in force field parameterisation.

This benchmarking exercise was critical in determining how accurately MD simulations could reproduce experimental observables and provided confidence in applying these methods more broadly. With this validation in place, the next step was to extend the approach to a wider range of lignin-derived molecules, examining how functional group differences and molecular shape affected bulk liquid diffusion.

Probing Functional Group Effects on Liquid-Phase Molecular Behaviour [2]

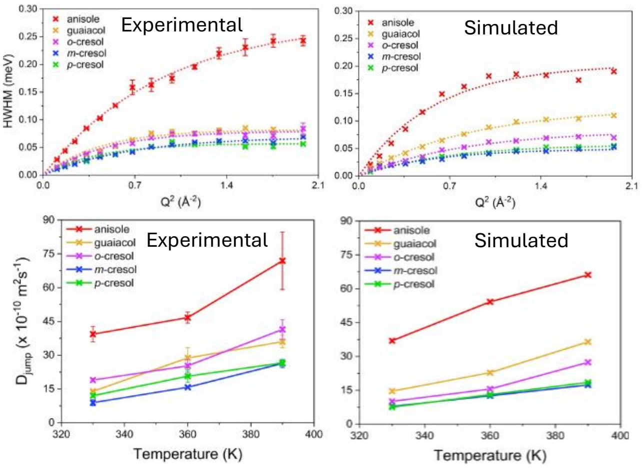

Figure 5. (top) Experimental and simulated QENS line broadenings compared along with the fitted jump diffusion model. (bottom) Experimental and simulated D_s values compared for each lignin derivative.

Building on the validated modelling approach established with *p*-cresol, the second study broadened the investigation to a suite of lignin-derived aromatics: anisole, guaiacol, and all three cresol isomers (*o*-, *m*-, and *p*-cresol)[2]. These molecules vary subtly in functional grouping and molecular shape—factors that influence how they interact with one another and with their environment in the liquid phase. Understanding these interactions and dynamics in the liquid phase is important if we are to understand the effects of confinement in the zeolite catalyst, and any differences as a function of pore structure and composition.

Quasielastic neutron scattering (QENS) experiments were performed to measure both translational and rotational motions of these molecules in the bulk liquid state, and the results were analysed alongside molecular dynamics (MD) simulations. A clear picture emerged: the presence or absence of hydroxyl and methoxy groups, as well as their position on the aromatic ring, significantly affected H-bonding interactions and resulting molecular mobility. Molecules like anisole, which lack a hydroxyl group, showed more rapid diffusion, while isomers with both hydroxyl and methyl groups in close proximity tended to exhibit slower movement due to stronger hydrogen bonding.

The MD simulations reproduced the main trends seen experimentally and gave diffusion coefficients in many cases within error of experiment, reinforcing the idea that even subtle differences in functional group arrangement can lead to marked variations in dynamical behaviour. Moreover, comparing shorter timescale dynamics (~100 ps captured by our QENS instrument) with longer-timescale behaviour in the simulations revealed how conventional analysis methods may sometimes oversimplify or misinterpret molecular motion.

This systematic study of functional group effects provided a robust foundation for understanding how molecular structure governs liquid-phase dynamics in lignin-derived systems. With this understanding in hand, the research could now move into more complex environments: exploring how these same molecules behave when confined within the pores of zeolite catalysts.

Mobility of Lignin Derivatives in Zeolite Catalysts [3,4]

With a clearer understanding of the liquid-phase behaviour of lignin-derived aromatics, the next phase of turned to how these molecules behave when confined within the microporous environments of industrial zeolite catalysts. Zeolites present complex, shape-selective environments where diffusion is no longer governed solely by molecular size and interactions with other liquids—but also by steric constraints, pore geometry, and interactions with acid sites in the framework.

Two studies were carried out in parallel, focusing on different subsets of lignin-derived molecules. One examined cresol isomers (*m*- and *p*-)[3], while the other focused on anisole and guaiacol[4]. In both cases, QENS was used to probe shorter-range motions such as molecular rotation and confined jump diffusion within the pores of commercial samples of H-Y and H-Beta zeolites. These experimental results were supported by molecular dynamics simulations, which provided additional insight into longer (ns) timescale diffusive behaviour beyond our QENS instruments.

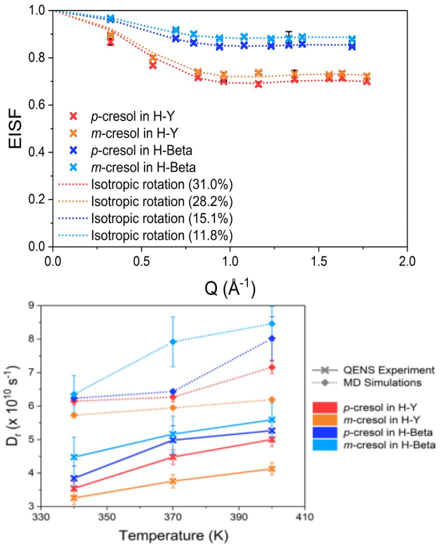

Figure 6. (top) QENS measurements showing mobile populations of cresol isomers in HY and H-Beta. (bottom) QENS/MD calculated diffusion coefficients of cresols in HY and H-Beta. [3]

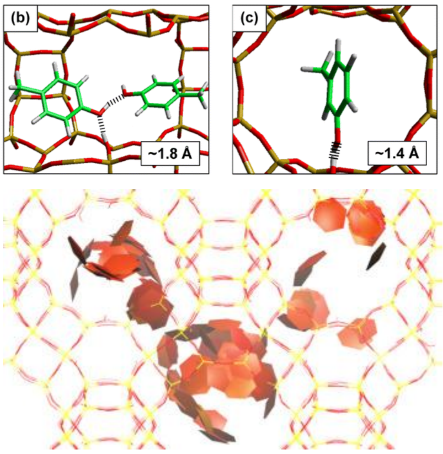

Figure 7 (top) Preferred orientations of cresol isomers in H-Beta and (bottom) orientation hindered cage confined diffusion of guaiacol in HY [4] and

Across both studies, several consistent trends emerged. Molecules with more compact or linear shapes, such as *p*-cresol and anisole, generally exhibited greater mobility than their bulkier or more strongly interacting counterparts like *m*-cresol or guaiacol. The larger pores of H-Y, allowed for higher populations of mobile molecules, whereas narrower channels in H-Beta imposed stronger steric constraints (figure 7, top). Of significant interest was the observation that the rotational rates of each molecule showed an inverse relationship to the diffusion coefficients, as an increased diffusivity led to more instances of adsorbate-adsorbate interactions, the dominant factor in hindering molecular rotation.

Importantly, mobility was not always shown to be a simple function of pore size, as H-Beta could enable continuous motion over longer distances in a single direction, while HY in some cases promoted more localised, almost ‘caged’ diffusion (figure 7, bottom).

Molecular shape and functional groups also played a major role in diffusion. For example, the hydroxyl group in guaiacol allowed it to form stronger interactions with acid sites, slowing its motion relative to anisole. Similarly, cresol isomers differed in their ability to align and orient within specific channels or form stabilising 180° H-bonds (figure 7, top), affecting how easily they move through the pore system.

Together, these studies painted a nuanced picture of how confinement, framework topology, and molecular functionality intersect to govern molecular mobility in zeolite catalysts. However, it still remained to probe the precise nature of the adsorption interactions between these molecules and the Brønsted acid sites within the zeolites. To address this, the final study turned to vibrational spectroscopy and quantum mechanical calculations to examine the local interactions in more detail.

Probing Molecular Level Adsorption Interactions [5]

Having explored how lignin-derived aromatics diffuse within zeolite catalysts, the final study turned to a more detailed understanding of how these molecules interact with the zeolite Brønsted acid sites which underpin the catalysis. These interactions govern how strongly molecules adsorb, how they are oriented within the pore, and how easily they can participate in catalytic reactions or desorb as products.

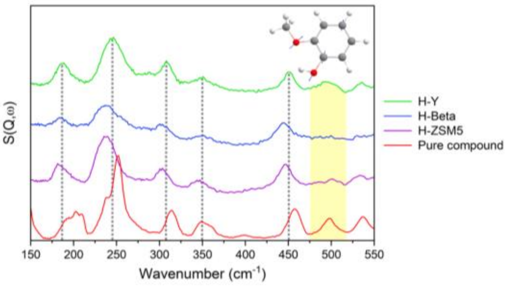

Figure 8. Example INS vibrational spectrum of guaiacol in different zeolites.

This investigation used inelastic neutron scattering (INS, vibrational spectroscopy with neutrons) in combination with density functional theory (DFT) calculations to probe the vibrational behaviour of the lignin derivatives when adsorbed within H-Y, H-Beta, and H-ZSM-5 zeolites[5]. By comparing the vibrational spectra of the adsorbed molecules with those of the pure compounds—and interpreting the changes with the aid of DFT phonon-mode calculations—the study revealed how molecular vibrations were altered upon adsorption, providing detailed insight into bonding geometries and strengths.

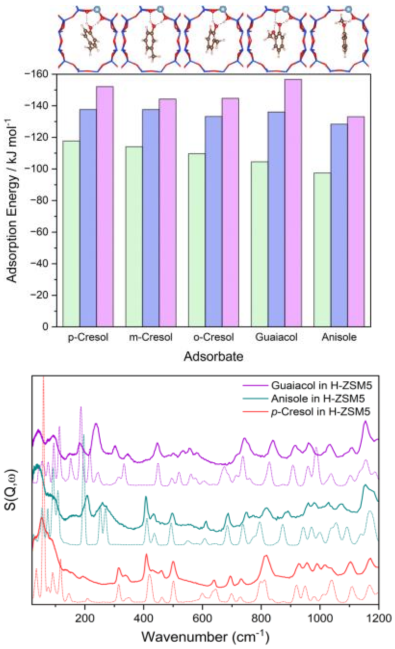

Figure 9. (top) adsorption energies and geometries of each lignin derivative in the zeolite frameworks. (bottom) Experimental and DFT generated INS spectra of derivatives in ZSM-5.

Strong adsorption for all zeolites shown in the form of both broadening and 'loss' of bending modes related to H-bonding groups in the experimental spectra (figure 8), and strong adsorption energies calculated in all DFT calculations (figure 9, top). The strongest adsorption was observed in smaller-pore zeolites, where stabilising interactions between the molecules and pore walls were enhanced. Most molecules favoured adsorption geometries involving dual hydrogen bonds—often forming five-membered ring structures with the acid sites—except for anisole, which lacked a hydroxyl group and interacted primarily through its methoxy group. These differences in interaction type and geometry were directly reflected in shifts and changes in intensity of key vibrational modes, which were reproduced surprisingly well by the DFT phonon calculations (figure 9, bottom).

Importantly, the study showed how adsorption strength and molecular orientation are closely linked to pore structure and functional group identity—factors that influence not only catalytic turnover but also the mobility trends observed in the diffusion studies. The findings of the study brought insights into adsorption interactions underpinning the dynamical behaviours explored throughout the fellowship and play a key role in linking molecular structure, adsorption strength, and mobility factors relevant to their conversion to useful chemicals.

Conclusions, Future Work and Industrial Collaboration

The Syd Andrew Fellowship has enabled me to lead an original and insightful series of studies, combining advanced experimental techniques with state-of-the-art molecular simulations to gain unique insights into the fundamental behaviours underpinning the catalytic conversion of lignin pyrolysis oil components into valuable chemicals. By focusing on catalysts already employed in existing infrastructure, this work aimed to contribute to efforts enabling a more timely and practical transition from fossil-derived feedstocks to sustainable, biomass-based alternatives—an essential objective for the future of the chemical industry. The research undertaken during the fellowship has laid important groundwork for future expansion into longer-timescale studies, and for establishing more direct correlations between molecular behaviour and catalytic performance—relationships that have typically been inferred indirectly.

An early element of industrial collaboration within the project involved engagement with Johnson Matthey, world leaders in the development of heterogeneous catalysts, whose input provided valuable perspective on the practical context and challenges in catalyst design. More recently, the foundational work has led to a new collaboration to perform similar work with Zeopore Technologies, who produce industrial-scale quantities of hierarchical micro–mesoporous catalysts. These materials are specifically engineered to overcome diffusion limitations and mitigate deactivation caused by pore blockage—issues especially pronounced when processing large, functionalised molecules from lignin pyrolysis.

~~Our ability to probe molecular-scale behaviour in confined environments, and to use these insights to now inform the design and optimisation of the next generation of catalysts—particularly those with hierarchical pore architectures—has been made possible through the studies carried out under this fellowship. This new industrial collaboration highlights the value of the fellowship not only in enabling novel science, but also in providing a compelling proof of concept that bridges fundamental research and real-world innovation. I am extremely grateful to have had the opportunity to further demonstrate how such research can seed meaningful industrial partnerships to address pressing challenges in catalyst development for more sustainable chemical processes.~~

References

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[2] "Experimental and modelling studies of the diffusion and rotational dynamics of simple lignin derivatives." *Journal of Molecular Liquids* 428 (2025): 127495.

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