

Selective coproduction of phenol and cresols from anisole in non-thermal plasma: Insights into transalkylation reactions

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Abstract: In this work, we study the non-catalytic transformation of anisole using a DBD plasma system at atmospheric pressure and room temperature. We found that a lower specific energy input benefits transalkylation reactions. The plausible reaction pathways were proposed through plasma optical emission spectroscopic diagnostics combined with a comprehensive analysis of major products, revealing the key role of transalkylation reactions in this plasma process.

Keywords: Non-thermal plasma, Bio-oil, Anisole, Phenol and cresols, Transalkylation reaction

1. Introduction

In the biodiesel industry, lignin is typically treated as waste residue and burned to generate energy [1, 2]. To improve the bio-based economy, the conversion of lignin into value-added chemicals has been well-advocated [3]. In recent years, the quest for alternative resources to replace fossil fuels in the synthesis of phenol and cresols has attracted public attention. Moreover, the latter usually requires rigorous conditions and faces several issues like waste disposal, corrosion, and catalyst deactivation by coking and sintering [4, 5].

Non-thermal plasma technology has been regarded as a promising alternative to conventional catalytic processes for the transformation of lignin-derived compounds at low temperatures and atmospheric pressure. Moreover, the transalkylation reaction induced in inert gas plasmas can enhance the stability of aromatic rings, i.e., by reducing the formation of polycyclic aromatic hydrocarbons (PAHs), this reaction considerably hinders carbon deposition. Besides, the transalkylation of anisole into cresols enables a direct conversion with 100% atom economy.

So far, very few efforts have been devoted to the transformation of lignin-derived compounds by non-thermal plasma, either with or without catalysts [6-8]. Moreover, little attention has been paid to the reaction mechanism, and there is no clear consensus regarding the role of transalkylation reactions play in the plasma process. This current lack of knowledge, together with the potential of plasma technology for this application, motivates the present study on anisole conversion in a dielectric barrier discharge (DBD) reactor. We believe that better insights into transalkylation reactions will not only allow for improved control of the selectivity in this plasma process but also be beneficial to its potential industrial application.

2. Experimental

Fig. 1 presents a scheme of the experimental setup in this study. The transalkylation ratios, specific energy input (SEI) and the efficiency of the plasma process are defined as:

$$\text{Transalkylation}_{\text{hydrocarbons}} (\%) = \frac{\text{moles of toluene}}{\text{moles of benzene}} \times 100 \quad (1)$$

$$\text{Transalkylation}_{\text{oxygenates}} (\%) = \frac{\text{moles of other oxygenates}}{\text{moles of phenol}} \times 100 \quad (2)$$

$$\text{SEI (kWh/m}^3) = \frac{P(\text{kW})}{\text{Total flow rate (m}^3/\text{h)}} \quad (3)$$

$$\text{Energy efficiency (g/kWh)} = \frac{\text{converted anisole (g/m}^3)}{\text{SEI (kWh/m}^3)} \quad (4)$$

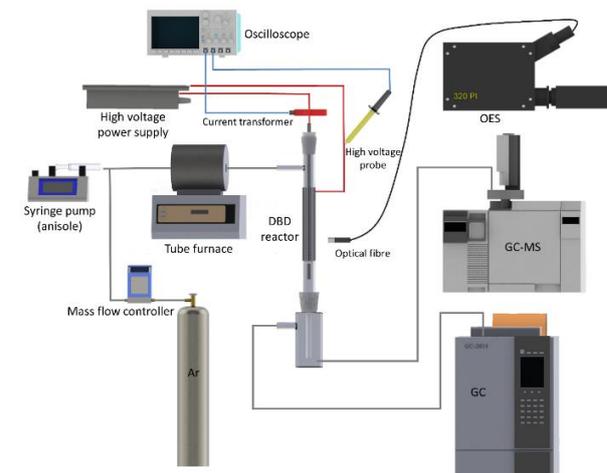


Fig. 1. Scheme of the experimental system.

3. Results and discussion

The influence of the anisole feed rate, Ar flow rate and discharge power on the plasma transformation of anisole has been evaluated in terms of anisole conversion, product selectivity and energy efficiency. The highest selectivity of cresols and phenol reached 55.4% and 58.0%, respectively. Gathering the results from different conditions, the transalkylation ratios of hydrocarbons and oxygenates showed higher values at lower anisole concentrations. Our results show that transalkylation reactions generally benefit from a lower specific energy input in this plasma process.

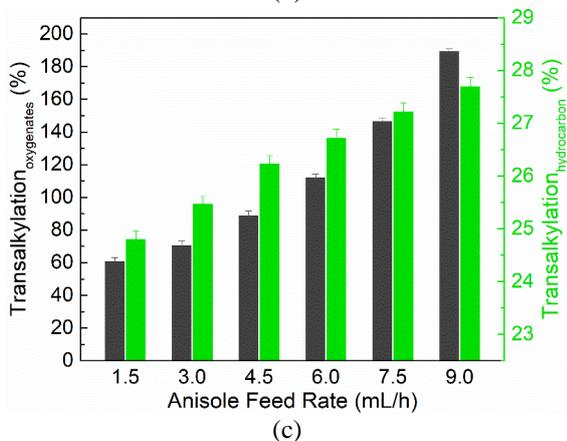
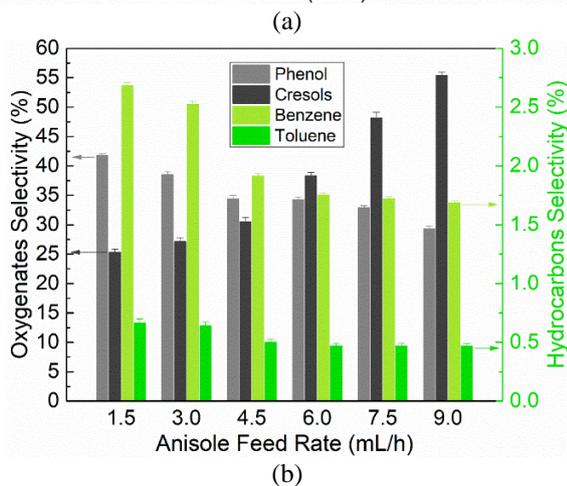
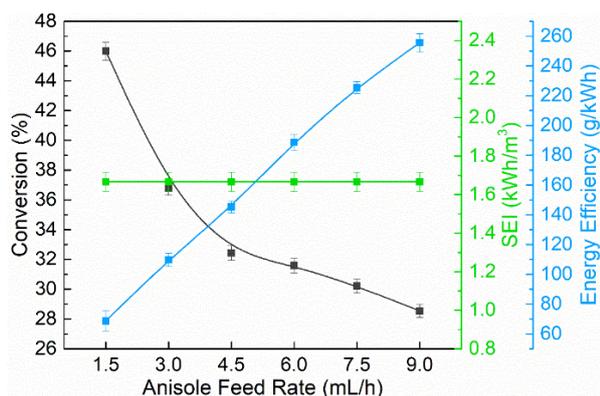


Fig. 2. Influence of anisole feed rate on (a) the conversion of anisole, SEI, energy efficiency; (b) the selectivity of major products; (c) the transalkylation ratios of hydrocarbons and oxygenated compounds (discharge power 10 W, Ar flow rate 100 mL/min).

A typical emission spectrum of anisole/Ar DBD plasma is presented in Fig. 3 where clear Ar-I spectral lines can be identified from 696.54 nm to 842.46 nm. In the plasma zone, ground-state Ar atoms were activated to the metastable state through drastic collision with highly energetic electrons. Based on the OES and GC analysis, the excited Ar atoms were considered as the key species in this plasma transformation process.



Compared with the traditional thermal/catalytic process, the presence of energetic electrons and excited Ar atoms in DBD plasma enables new reaction routes leading to species such as those shown in R1 and R2.

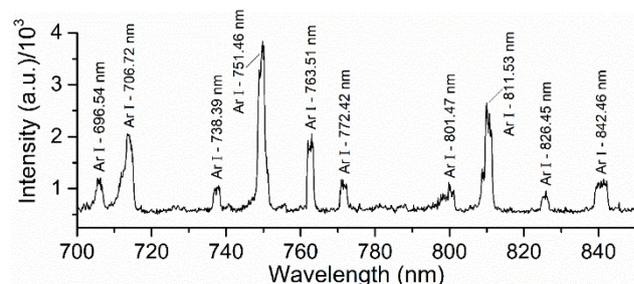
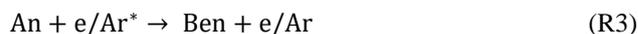


Fig. 3. The optical emission spectrum of anisole/Ar plasma (discharge power 10 W, Ar flow rate 100 mL/min, anisole feed rate 3.0 mL/h, spectral resolution 0.05 nm, grating 600 g/mm, exposure time 100 ms).

4. Reaction mechanism

The reaction pathways of the transformation process were proposed based on the bond dissociation energies in anisole that were found to follow the ordering Ar-OH > ArOCH₂-H > Ar-OMe > ArO-H > ArO-Me (Ar: aryl group). Based on previous studies [9-11] and the results here presented, transalkylation was considered as the dominant reaction: (An: anisole, Ben: benzene, Tol: toluene, Ph: phenol, Cr: cresol isomers, MA: methylanisole isomers)



Cresol and phenol molecules are generated by bimolecular routes (R4-R7). It is worth mentioning that these reactions are likely to consist of several elementary steps. In addition, some other reaction routes, including demethoxylation and demethylation, may co-exist to form aromatic compounds. Through transalkylation reactions, the majority of the methyl groups were retained, and the conversion of anisole into cresols was achieved with 100% atom economy. According to our findings, insights into plausible reaction pathways for this plasma process were proposed (see Fig. 4).

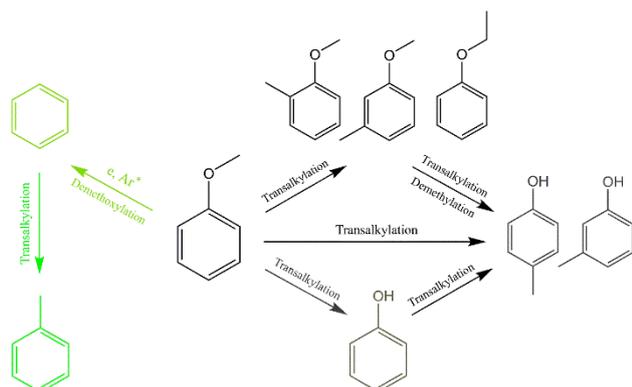


Fig. 4. Proposed reaction pathways of the anisole transformation in Ar plasma.

5. Conclusion

In this work, we presented a detailed investigation of the non-catalytic conversion of anisole by a bench-scale DBD plasma system at ambient pressure and room temperature. It was found that the conversion of anisole, the selectivity of major products and energy efficiency of the plasma process can be tuned by varying the operating conditions including anisole concentration, Ar flow rate and discharge power. By investigating the transalkylation ratios, the transalkylation reactions were found to be favoured by a low energy density environment in non-thermal plasma. In addition, Ar metastable atoms were considered as key species in this process. It was attributed to the transalkylation reactions that only a trace amount of condensed aromatics was observed in this process, which effectively prevented the formation of chars. The position of initial cleavage in anisole molecule may preferentially occur at the ArO-Me bond. Plausible reaction pathways for this process has been discussed and proposed.

6. References

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