

JUNE 2025

# RENEWABLE ENERGY, BIOMASS & SUSTAINABILITY

ISSN: 2683-2658

Vol. 7, No. 1



**RE&S**



ASOCIACIÓN LATINOAMERICANA DE DESARROLLO

**ALDESER**

SUSTENTABLE Y ENERGÍAS RENOVABLES

## **Renewable Energy, Biomass & Sustainability**

### **Vol. 7 No. 1 (2025)**

Published: June 11, 2025

Renewable Energy, Biomass & Sustainability, Vol. 7, No. 1, June 2025, is a biannual publication, published and edited by Asociación Latinoamericana de Desarrollo Sustentable y Energías Renovables A.C. (ALDESER), Sur 4 No. 270, Colonia Centro, C.P. 94300, Orizaba, Veracruz, Mexico, Tel. 2722372285, Web Page: <https://aldeser.org/revistas.html> and email address: [secretariat@aldeser.org](mailto:secretariat@aldeser.org).

The Reservation of Rights of Exclusive Use Certificate No.: 04-2025-060617423800-102, ISSN: 2683-2658, are both granted by the Instituto Nacional del Derecho de Autor (INDAUTOR, Mexico). Responsible for the last update of this issue: Andrea Alvarado Vallejo. Date of last modification, June 18, 2025.

The papers published in the journal are subject to peer review and their content is the author's exclusive responsibility and does not necessarily represent the point of view of the Association or the editor.

## Table of Contents

**Study of the social significance of water and its treatment in La Reforma, Alto Lucero de Gutiérrez Barrios, Veracruz, Mexico: interests and opportunities** **1-10**

Irma Zitácuaro-Contreras, Aarón López-Roldán, Sergio Aurelio Zamora-Castro, José Luis Marín-Muñiz, Juan Antonio Triana-Tello, Neira Sánchez Zárate, Luis Manuel Álvarez-Hernández, Karina Elizabeth Martínez-Aguilar

**Hydrodeoxygenation of anisole to produce value-added products: ortho-, meta-, para-cresol** **11-21**

Leonor Angélica Guerrero Zúñiga, Ana Cristina Ramirez-Gallardo, María Fernanda López Sánchez, Isidoro Garcia-Cruz

# Study of the social significance of water and its treatment in La Reforma, Alto Lucero de Gutiérrez Barrios, Veracruz, Mexico: interests and opportunities

Irma Zitácuaro-Contreras <sup>1</sup>, Aarón López-Roldán <sup>1</sup>, Sergio Zamora-Castro <sup>2</sup>, José Luis Marín-Muñiz <sup>3,\*</sup>, Juan Antonio Triana-Tello <sup>4</sup>, Neira Sánchez-Zárate <sup>3</sup>, Luis Manuel Álvarez-Hernández <sup>1</sup>, Karina Elizabeth Martínez-Aguilar <sup>1</sup>

<sup>1</sup> Posgrado Desarrollo Regional Sustentable. El colegio de Veracruz, Xalapa, Veracruz, México.

<sup>2</sup> Facultad de Ingeniería, Construcción y Hábitat. Universidad Veracruzana. Boca del Río, Veracruz, México.

<sup>3</sup> Ingeniería Ambiental. Tecnológico Nacional de México/Instituto Tecnológico Superior de Misantla, Veracruz, México.

<sup>4</sup> Facultad de Ingeniería Mecánica y Ciencias Navales. Universidad Veracruzana. Veracruz, México.

\* Corresponding author: [jmarinm@itsm.edu.mx](mailto:jmarinm@itsm.edu.mx); Tel.: (+52 2281624680)

Received: May 11, 2025

Accepted: June 4, 2025

Published: June 11, 2025

DOI: <https://doi.org/10.56845/rebs.v7i1.453>

**Abstract:** The treatment of wastewater in rural areas presents a multifaceted challenge that requires collaboration among government entities, academic institutions, and community members. In Mexico, over 184,000 rural communities lack adequate sanitation systems, leading to significant social and environmental issues. Non-conventional technologies, such as constructed wetlands (CWs) present favorable solutions for rural communities due to their environmental, economic, and social advantages. This study employed documentary research, participant observation, and structured interviews conducted door-to-door in the La Reforma community, located in Alto Lucero, Veracruz, Mexico. The aim was to assess residents' knowledge regarding environmental issues and the management of the community's wastewater, as well as their interest in adopting a non-conventional sanitation system, specifically a treatment wetland. The findings indicate that while the population is aware of water pollution, they lack in-depth knowledge regarding specific details. Although they are unfamiliar with sanitation infrastructure based on constructed wetlands, they expressed a desire for a treatment system when introduced to basic concepts and showed willingness to collaborate on the project. The initiative enjoys social acceptance, and the next phase will involve governmental coordination for implementation, with municipal authorities and academic participation identified as key stakeholders.

**Keywords:** Wastewater treatment, social participation, communal benefits, constructed wetlands.

## Introduction

The development of rural communities through economic initiatives has focused on enhancing health services, food security, poverty alleviation, the delivery of essential services, and productivity, particularly within the agricultural, livestock, and forestry sectors (Government of Mexico, 2022). To support these goals, there are institutional public policies in place at both the international level, such as those from the United Nations (UN), and at the national level through programs implemented by Mexico's government secretariats. However, the challenges posed by limited economic resources and the widespread dispersion of rural communities in Mexico, which numbered 184,000 and accounted for 97.7% of the total as of 2020, complicate the delivery of sanitation services. These rural areas are home to 26.6 million individuals, representing 21% of the national population, with women making up 50.6% of this demographic. This is particularly significant, as they are often the most adversely affected by inadequate access to quality water for household needs.

Among the Mexican states with the highest percentage of rural areas, the order, from highest to lowest, is as follows: Chiapas at 50.8%, Oaxaca at 50.5%, Hidalgo at 42.7%, Tabasco at 41.5%, Guerrero at 40.3%, Veracruz at 38.3%, Zacatecas at 36.7%, and San Luis Potosí at 32.8% (Government of Mexico, 2022; INEGI, 2024). This situation has resulted in the identification of a significant issue in rural areas: the lack and poor quality of water, which accounted for 18.4% of the ten most prevalent problems in these regions (INEGI, 2020). The National Institute of Statistics, Geography and Informatics (INEGI) estimates that over 57,000 rural areas (31.0% of the total) are at risk due to the presence of polluting agents in the air, land, or bodies of water. Furthermore, sewage management presents a challenge, as open dumping aggravates public health issues through direct exposure to contamination sources. Currently, there are records of 22,600 rural localities (12.3%) with access to a public drainage system, where approximately 11.1 million people (41.7%) reside. This indicates that 77.5% of localities lack a sewage system, and there is no available data for the remaining 10.2%. Consequently, an estimated 15.5 million Mexicans do not have access to sewage services.

In a different context, data from the Government of Mexico (2022) indicates that Veracruz ranks among the states with the highest number of rural communities. However, the region's diverse topography leads to a significant dispersion of

these communities, posing challenges in providing essential services, including sewage and wastewater treatment. Veracruz stands fifth in the nation in terms of community count, encompassing a total of 19,500, which represents 10.6% of the country's total. This area is home to 38% of Veracruz's population, amounting to approximately 8.1 million people (INEGI, 2020). To foster rural development concerning sanitation and enhance health management, particularly for children, it is crucial to reduce pollution from untreated wastewater discharges by establishing the necessary infrastructure to purify contaminants. In this regard, the National Water Commission (CONAGUA) (2023) reports that Veracruz operates 94 conventional treatment plants that handle a flow rate of 4,380.8 liters per second. These plants employ various processes, including biological discs, biological filters, stabilization lagoons, aerated lagoons, activated sludge, primary treatment, advanced primary treatment, upflow anaerobic reactors (U.A.S.B.), enzymatic reactors, Imhoff tanks, and septic tanks (CONAGUA, 2025). Treatment wetlands, also known as constructed wetlands, represent non-traditional wastewater management systems in Mexico. However, in Veracruz, the number of reported treatment wetlands is limited according to CONAGUA, primarily because most systems in various communities have been implemented through academic projects.

Notably, the 94 operational treatment plants in Veracruz serve only 0.5% of the total communities in the state. This statistic highlights the significant challenge posed by inadequate sanitation infrastructure, which results in water source contamination and a rise in waterborne diseases. Given the scarcity of financial resources and the dispersed nature of rural populations, treatment wetlands emerge as a viable alternative for wastewater treatment in these areas. These systems are included in the officially recognized sanitation systems documented by CONAGUA in its statistics. Consequently, these systems are regarded as a public policy, as the operational guidelines for allocating financial resources include the development of systems based on natural wetlands with pits (CONAGUA, 2025).

Sanitation wetlands are considered alternative systems; they represent ecotechnologies that operate similarly to natural wetlands. Both systems offer essential environmental services, notably the removal of contaminants through the cultivation of plants or phytoremediation processes. This involves the use of macrophytes and ornamental species that, through research, have demonstrated their adaptability to wetland ecosystems and their effectiveness in contaminant removal at pilot, household, and community scales. Additionally, these processes are enhanced by employing substrates that promote the proliferation of microorganisms or aerobic bacterial processes in the rhizosphere of plants, alongside the carbon cycling that occurs similarly to natural wetlands (Plaza de los Reyes *et al.*, 2011; Sandoval-Herazo *et al.*, 2019; Zamora-Castro *et al.*, 2025).

Sanitation wetlands offer several significant benefits, particularly in terms of sustainable management. Environmentally, they contribute to returning water of a higher quality to the ecosystem than what originally entered the system. Additionally, these wetlands utilize local materials and native plants, minimizing any adverse environmental impact. From a social standpoint, they foster community engagement by building social capital through outreach initiatives, which helps elevate the recognition of civic groups responsible for managing sanitation infrastructure. Evidence suggests that bioengineered wetlands are conducive to community involvement in their operation and maintenance. Economically, they stand out as a cost-effective alternative, as they do not necessitate substantial investments from government, academic, or community sources; their construction costs are significantly lower than those of traditional infrastructure (Hernández, 2016; Zitácuaro-Contreras *et al.*, 2021). These characteristics make sanitation wetlands particularly viable for implementation in rural areas where government funding may be limited.

In the State of Veracruz, the municipality of Alto Lucero de Gutiérrez Barrios faces significant wastewater challenges, particularly in the area of La Reforma, which is home to 1,335 residents. These inhabitants currently lack access to wastewater treatment services, leading to severe water and soil contamination issues. While alternative solutions could be introduced through effective governance strategies, it is crucial first to understand the principles of ecotechnology and to assess the interest, commitment, and potential for social participation within the La Reforma community. Accordingly, this study aims to explore the residents' awareness of environmental issues and the management of local wastewater, as well as their willingness to implement an unconventional sanitation system.

## Materials and Methods

### Study Area

The study was conducted in the rural locality of La Reforma, situated in the municipality of Alto Lucero de Gutiérrez Barrios, Veracruz, Mexico (see Figure 1). This area is located in the central part of the state of Veracruz at coordinates 19°35'46" N, 96°38'02" W, and is positioned at an altitude of 684 meters above sea level (PueblosAmerica, 2024). It lies approximately 11 km from the municipal seat of Alto Lucero.

As of 2020, the population of La Reforma was 1,330, with a slight male predominance at 50.7%, while females constituted just under 49.3%. The fertility rate in the area is 2.35, and recent census data indicates a population decline of 4.4% over the last 15 years. Notably, only 6.8% of the population is under 5 years old, whereas 23.3% are aged 60 and older. The community consists of 464 homes, which enjoy access to electricity (99.78%), water (99.57%), and sanitation services (99.14%). However, sewage coverage details are unspecified, and the area lacks sanitation infrastructure (PueblosAmerica, 2024).

There is no documented account of the indigenous population; however, education rates remain low (see Table 1), and primary education completion rates fall short of expectations, despite a decrease in illiteracy rates over the past decade. Access to higher education is restricted due to insufficient educational infrastructure. Economic activities in the region include agriculture, livestock farming, and commerce, particularly in the production of mangoes and passion fruit.



Figure 1. Location of the community La Reforma, Alto Lucero, Veracruz, Mexico.

Table 1. Schooling in La Reforma, Alto Lucero, Veracruz.

	2020	2010
Illiterate population (Total)	15.96%	18.72%
Illiterate population (hombres)	8.09%	19.25%
Illiterate population (mujeres)	7.87%	18.18%
level of schooling (Total)	5.96	5.14
level of schooling (man)	6.11	5.04
level of schooling (woman)	5.8	4.24

Source: PueblosAmerica (2024).

## Methodology

The research employed a mixed-methods approach, combining documentary research with qualitative and quantitative data analysis (see Figure 2). This exploratory study utilized measurement instruments, including a structured interview format designed for house-to-house administration by a group of 11 graduate students. Statistical analysis was conducted to process the data, employing descriptive measures of the variables (Casado, 2007).

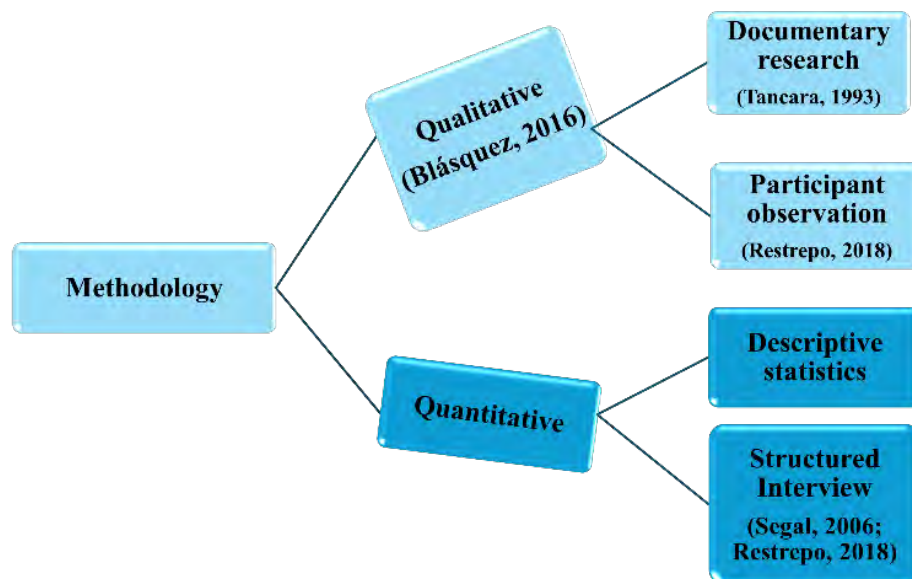


Figure 2. Methodological Process.

To determine the sample size for the interviews, the finite population equation was applied, taking into account the total number of homes in the community (464) (Rojas *et al.* 2014) (equation 1;  $n \geq (Nz^{2_{1-a/2}}PQ / z^{2_{1-a/2}}PQ + d^2(N-1))$ ). Here,  $n$  represents the sample size,  $N$  denotes the population size,  $z$  is the value corresponding to the Gaussian distribution (1.96),  $p$  signifies the estimated population proportion, and  $d$  denotes the precision level (0.05), with a confidence level of 95%. This calculation resulted in a sample size of 107 subjects, which corresponds to the number of interviews conducted.

## Results and Discussion

The absence of wastewater treatment in the La Reforma community has led to a widespread practice of reusing wastewater for agricultural irrigation. However, the absence of proper treatment has led to unsanitary conditions that compromise the quality of agricultural produce and pose significant public health risks for farmers, consumers, and the wider community. This study included an investigation into the awareness among La Reforma residents regarding the environmental conditions related to water and the disposal of the community's wastewater. Additionally, it aimed to gauge potential interest in collaborating with academic institutions and government authorities to establish a wastewater treatment system for urban public sources. Such an initiative is essential to mitigate the soil contamination in agriculture areas and to protect the groundwater tables of the Actopan Valley aquifer (Conagua, 2024). This contamination occurs by infiltrates the subsoil, either by gravity through unlined channels or through its reuse in agricultural irrigation.

To assess the population's knowledge, we began by identifying the sample group that provided the basis for our results. The interviews were conducted in the morning, leading to a predominance of female participants, although males were not excluded and represented just over a quarter of the sample (Figure 3a). The age of participants ranged from 15 to 95 years, with the majority—50%—falling within the 46 to 65 age brackets. Notably, among the 6% of adults aged 76

to 95, many live alone. Consequently, the issue of contaminated water discharge is not significant, as this demographic constitutes a very small percentage (Figure 3b).

The reported level of education among the population is primary education (PueblosAmerica, 2024), which aligns with the findings from the structured interview (Figure 3c), where 49% of participants indicated they have a primary education. This should not raise concerns, as the textbooks cover fundamental topics such as the responsible use of natural resources, particularly water, which is emphasized as essential for resource preservation (Zitácuaro-Contreras *et al.*, 2024). This is further supported by environmental education theory, which highlights its connection to formal education (Gaudiano, 2001). This theory suggests that environmental education has been enhanced through teacher training in environmental issues and the sustainable use of natural resources. Therefore, the educational level enables the application of more effective resource practices, which can also lead to sustainability (Fedulova *et al.*, 2019). Given these findings, the population possesses the knowledge to comprehend the origins of water pollution and the implications of discharging untreated water. The key lies in actively engaging them in the pursuit of solutions to address their pollution challenges.

One key factor influencing wastewater generation is the occupation of the population. In the sampled interviews, the predominant activity is homemaking, accounting for 50% (Figure 3d), which aligns with the observation that the majority of respondents are female (Figure 3a). This is followed by agricultural work, representing 17%, which is significant as many individuals are typically employed in the fields during the morning hours. However, interviews were conducted exclusively in the morning due to safety concerns on the roads in the area. Notably, there is no industrial activity present, which contributes to the relatively low severity of the pollution issue, as industry is the economic sector responsible for the highest levels of pollutants (CONAGUA, 2022). Additionally, given that this is a rural community with a population of fewer than 2,500 inhabitants, economic activities exert little influence on pollutant generation. Nevertheless, it is crucial to recognize that community wastewater discharges can pose infection risks for residents as well as for local crops, flora, and fauna.

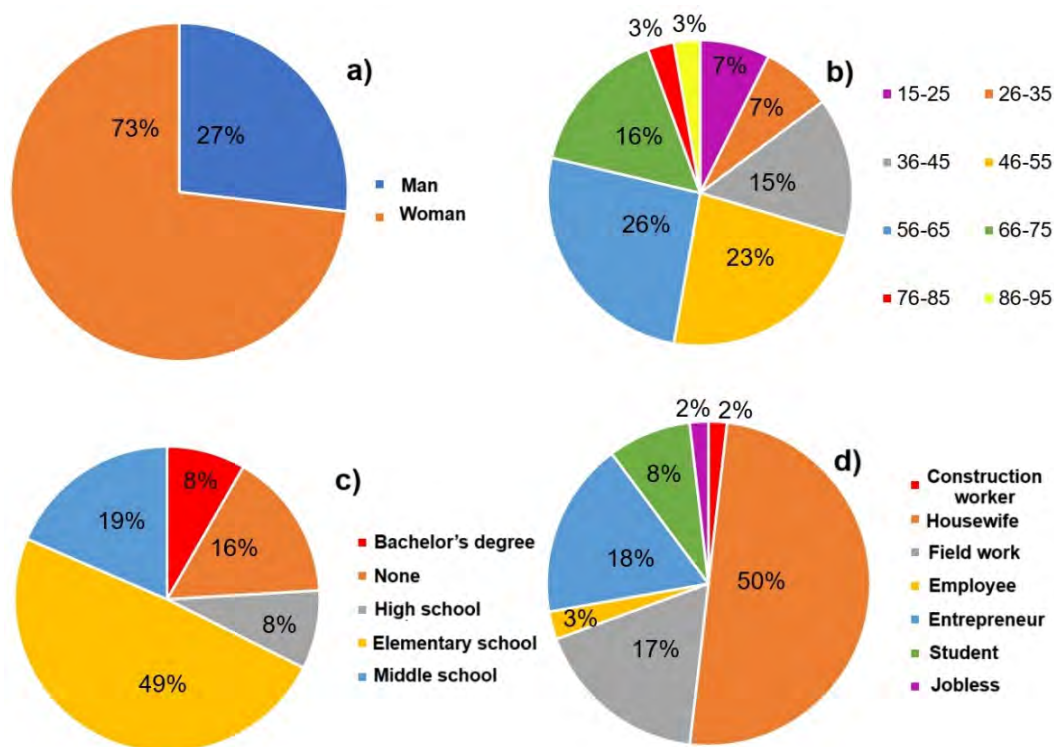


Figure 3. The figure presents the following variables: a) Sex, b) age, c) educational level, and d) occupation.

The second section involved analyzing the data to assess whether the interviewed participants were aware of the destination of the wastewater generated in homes in La Reforma. Due to the absence of drainage coverage data, the findings from the measurement instrument indicated that a significant majority (93%) of homes are connected to the

drainage network (see Figure 4a). Additionally, 72% of respondents were able to identify the discharge points (Figure 4b). These discharge points are located on the outskirts of the town and function through gravity runoff. One of the points involves collecting the water in a well, from which it is subsequently reused for certain agricultural irrigation activities via pumping.

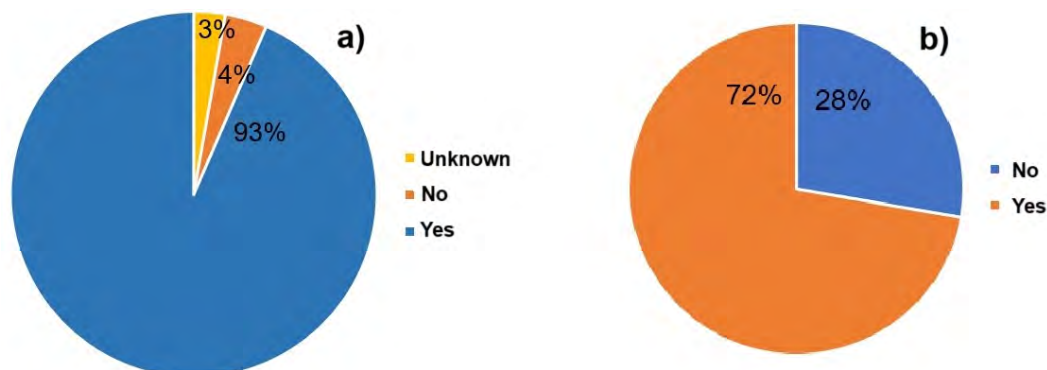


Figure 4. a) House connected to the sewer, and b) destination of the water discharge.

Once it has been established that the homes are connected to a sewer service, the implementation of a wastewater treatment system can proceed. However, this implementation must be supported by community involvement to ensure the project's sustainability in both operation and maintenance. Furthermore, when asked if measures are being taken to prevent water pollution, 60% of respondents indicated that they do not engage in any such activities. This suggests that while awareness of environmental issues may exist, practical application has not been realized. This situation is not directly related to education; at the primary level, environmental topics concerning the conservation of natural resources are indeed taught. According to Piaget (1991), children at this stage exhibit characteristics that foster an understanding of environmental responsibility and the ability to conceptualize problems and translate them into solutions through practical action in their social environments. Additionally, it is evident that treated water can have a secondary use. As illustrated in Figure 5b, opinions expressed indicate that treated water can be reused at home for various purposes, such as washing sidewalks, watering plants, cleaning cars, and maintaining domestic and animal areas.

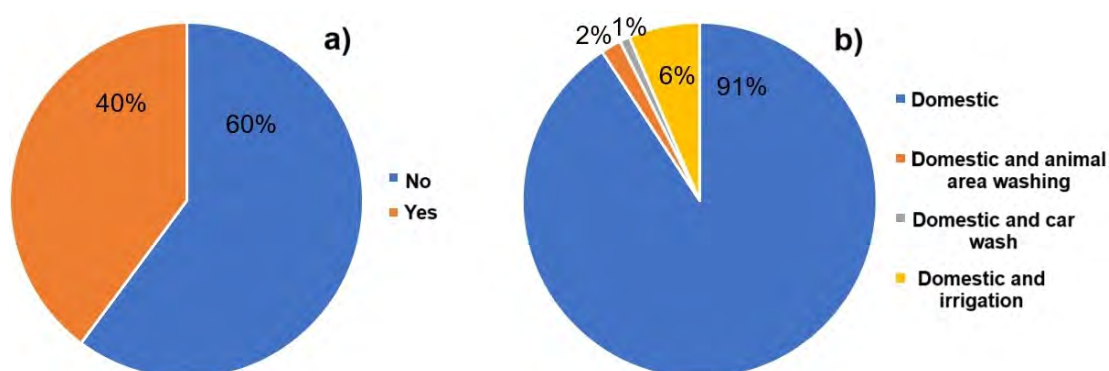


Figure 5. The questions posed included: a) Are you taking any measures to prevent water pollution? and b) What potential uses could treated wastewater have?

Another analytical approach involved creating opinion clouds to capture what certain environmental issues signify. Water quality is associated with the positive aspects of water use essential for sustaining life and ensuring that it is safe for consumption (see Figure 6a). Interviewees expressed that caring for water represents life itself; it is viewed as a necessity and an act of stewardship. However, opinions vary widely, with some demonstrating a lack of engagement and highlighting an insufficient understanding of how to protect this vital resource. This underscores the need for awareness-raising initiatives focused on water culture (refer to Figure 6b).



The next mandatory question followed a brief explanation of constructed wetlands, including images and highlighting their benefits for wastewater sanitation. Participants were then asked if they would be willing to assist in the construction of a treatment wetland, either through active participation or by providing materials. It was encouraging to discover that 95% of the sample expressed their willingness to contribute to the project. While community and academic involvement is assured, government participation is still in the planning stages.

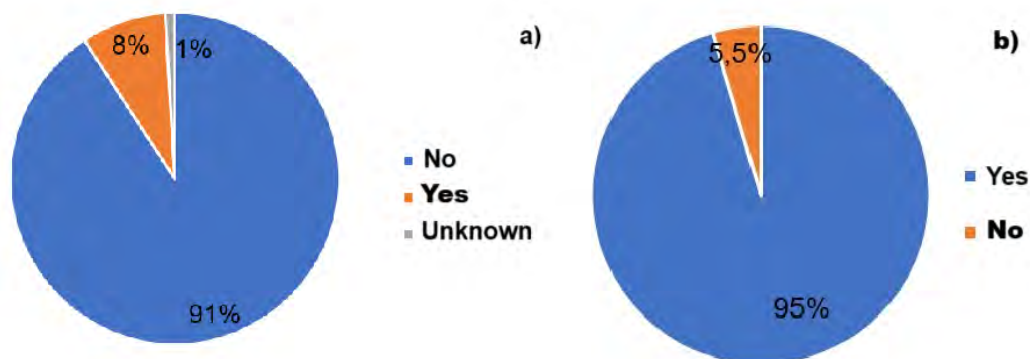


Figure 8. a) Are you familiar with the concept of a wetland? b) Would you be willing to take part in the construction of a treatment wetland?

The evidence presented indicates a general understanding of topics related to water, including its quality, distribution, and conventional conservation practices. However, this knowledge is not widespread; technical concepts, the environmental benefits these systems provide, and their social advantages remain largely unknown. Additionally, the motivations for social participation and the development of social capital are not well understood. Similarly, the collaborative efforts required for the construction, operation, and maintenance of these systems are unfamiliar to many. Consequently, the successful implementation of a sanitation project necessitates the engagement of the community and the cultivation of the essential capital for effective system management. In the initial phase of the sanitation project in the La Reforma community, social interest in the initiative has been documented.

It is important to highlight that studies of this nature are essential for advancing proposals aimed at addressing local issues. In the State of Veracruz, the Ministry of the Environment (SEDEMA) has been actively promoting financial support for environmental development over the past several years. One promising option for such support projects is the installation of sustainable water purification systems. These initiatives aim to tackle community challenges through collaboration with both society and academia. Consequently, having access to this information facilitates the development of preliminary projects for participation in relevant funding opportunities. Furthermore, it underscores the collaborative efforts that can be undertaken by all stakeholders for the greater good: a healthy environment and a responsible society.

Future studies could explore the areas suitable for intervention in treatment systems, as well as the establishment of leadership groups to support the various activities involved in the process. These activities may include system design, determining the strategic implementation point where the water to be treated arrives via gravity, training operators, monitoring resources, and conducting awareness-raising initiatives, among others.

## Conclusions

The implementation of sanitation systems utilizing environmentally friendly ecotechnologies, such as constructed wetlands, is particularly well-suited for rural areas. The lack of awareness regarding ecotechnology hinders the generation of interest necessary to promote the use of government resources for the implementation of systems that adhere to the guidelines outlined in this public policy. The study revealed that while there is a general understanding of issues related to water resource preservation, this knowledge does not translate into a demand for sanitation infrastructure, nor does it foster community-driven construction efforts. Wastewater treatment solutions in rural areas present a viable option, provided that the population is informed about the requirements, as these systems are relatively straightforward to implement from environmental, economic, and social perspectives. Management should

be integrated to enable municipal authorities to implement these systems in alignment with the powers granted to them by the Mexican Constitution. In the state of Veracruz, there are various projects funded by the Ministry of the Environment of the state government, operated and maintained by organized civil society and academia. These initiatives adhere to a governance framework that has proven effective and contributes to a healthy environment, a fundamental human right established in the Constitution. The research conducted in this study highlights the necessity for awareness-raising actions focused on water culture, the implementation of eco-technologies for water treatment, and understanding the impacts of using wastewater for agriculture. The public's interest in the development of eco-technologies serves as an important first step in shaping these initiatives.

**Acknowledgments and Funding:** We extend our heartfelt gratitude to SECIHTI in Mexico for their generous funding of scholarships for graduate studies. Additionally, we would like to acknowledge the contributions of the graduate students in Sustainable Regional Development who supported us during the interview phase: Nelson Andrés Losada Rodríguez, Yennis Ramos Pérez, Damaris González Rivadeneyra, Claudia Muñoz Aguilar, and David Mejía Escobar.

**Author contributions:** I.Z-C, and A.L-R: writing, design, data collection, editing. L.M.A-H and K.E.M-A: data collection and capture, and analysis of data. J.L.M-M conceptualization, design, supervision. S.A.Z-C., N.Z-S, and J.A.T-T: Provide materials and edition of the methodology.

## References

- Blásquez, M. L. I. (2016). La etnografía: una aproximación metodológica para la comprensión de los procesos sociales. En M. Guereca, T. (Ed), *Guía para la investigación cualitativa: etnografía, estudio de caso e historia de vida*. Universidad Autónoma Metropolitana.
- Comisión Nacional del Agua (CONAGUA). (2022). *Numeragua*. Gobierno de México.
- Comisión Nacional del Agua (CONAGUA). (2023). *Inventario de Plantas Municipales de Potabilización y de Tratamiento de Aguas Residuales en Operación*. México. Gobierno de México.
- Comisión Nacional del Agua (CONAGUA). (2025). *REGLAS de Operación del Programa de Agua Potable, Drenaje y Tratamiento (PROAGUA), a cargo de la Comisión Nacional del Agua, aplicables a partir de 2025*. Gobierno de México,
- Comisión Nacional del Agua (CONAGUA). (2024). *Actualización de la disponibilidad media anual de agua en el acuífero Valle de Actopan (3005), Estado de Veracruz*. Gobierno de México.
- Fedulova, I., Ivanova, V., Atjukova, O., y Nosov, V. (2019). Inclusive education as a basis for sustainable development of society. *Journal of social studies education research*, 10(3), 118-135.
- Gaudiano, E. G. (2001). Otra lectura a la historia de la educación ambiental en América Latina y el Caribe. *Desenvolvimento e Meio ambiente*, 3, 141-158.
- Gobierno de México (2022). ¿Qué nos dice el Censo de Población sobre la juventud rural de nuestro país?, Consultado el 25 de febrero de 2025 <https://www.gob.mx/siap/articulos/que-nos-dice-el-censo-de-poblacion-sobre-la-juventud-rural-de-nuestro-pais?idiom=es#:~:text=M%C3%A9xico%20cuenta%20con%20189%2C432%20localidades%20a%20lo,del%20total%20de%20las%20localidades%20del%20pa%C3%ADs.&text=Asimismo%2C%20la%20poblaci%C3%B3n%20joven%20en%20las%20localidades,del%2017%20de%20la%20poblaci%C3%B3n%20rural%20total>
- Hernández, A. M. E. (2016). Humedales ornamentales con participación comunitaria para el saneamiento de aguas municipales en México. *RINDERESU*, 1(2): 01-12.
- Instituto Nacional de Estadística y Geografía (INEGI) (2024). *¿Qué hay en las localidades rurales de México?* Consultado el 20 de enero de 2025. [https://www.inegi.org.mx/contenidos/productos/prod\\_serv/contenidos/espanol/bvinegi/productos/nueva\\_estruc/889463915119.pdf](https://www.inegi.org.mx/contenidos/productos/prod_serv/contenidos/espanol/bvinegi/productos/nueva_estruc/889463915119.pdf)
- Instituto Nacional de Estadística y Geografía (INEGI) (2024). *Información por entidad Veracruz*. Consultado el 28 de enero de 2025 <https://cuentame.inegi.org.mx/monografias/informacion/ver/poblacion/default.aspx?tema=me&e=30>
- Martínez-Aguilar, K.E., Marín-Muñiz, J.L., Álvarez-Hernández, L.M., Defín, E., Zamora-Castro, S. (2024). Current status of wastewater treatment through large-scale treatment wetlands in the state of Veracruz, Mexico. *Renewable Energy, Biomass & Sustainability (REB&S)*, 6(2), 32-42. <https://doi.org/10.56845/rebs.v6i2.105>
- Piaget, Jean (1991). *Seis estudios de psicología*. España. Labor. 199 p.
- Plaza de los Reyes, C. Vera, L., Salvato, M., Borin, M., & Vidal, G. (2011). Consideraciones para la eliminación del nitrógeno en humedales artificiales. *Tecnología del agua*, 31(330), 40-49.
- Rojas, O., Sáez, K., Martínez, C., Jaque, E. (2014). Post-catastrophe social-environmental effects in vulnerable coastal areas affected by the tsunami of 02/27/2010 in Chile. *Interciencia*, 39, 383–390.
- Segal, D. L., Coolidge, F. L., O'Riley, A., y Heinz, B. A. (2006). Structured and semistructured interviews. *Clinician's handbook of adult behavioral assessment*. 121-144.
- Restrepo, E. (2018). *Etnografía: alcances, técnicas y éticas*. Universidad Nacional Mayor de San Marcos.
- Sandoval, L., Zamora-Castro, S. A., Vidal-Álvarez, M., & Marín-Muñiz, J. L. (2019). Role of wetland plants and use of ornamental flowering plants in constructed wetlands for wastewater treatment: A review. *Applied Sciences*, 9(4), 685.
- Tancara, C. (1993). La investigación documental. *Temas sociales*, (17), 91-106.
- Zamora-Castro, S. A., González-Moreno, H. R., Hernández-Orduña, M. G., Zitácuaro-Contreras, I., & Marín-Muñiz, J. L. (2025). Environmental Assessment of a Constructed Wetland with Ornamental Vegetation for Wastewater Treatment: A Sustainable Option for Neighborhoods (The Case of Veracruz, Mexico). *World*, 6(2), 50.

- 
- Zitácuaro-Contreras, I., Vidal-Álvarez, M., Hernández y Orduña, M. G., Zamora-Castro, S. A., Betanzo-Torres, E. A., Marín-Muñiz, J. L., & Sandoval-Herazo, L. C. (2021). Environmental, Economic, and Social Potentialities of Ornamental Vegetation Cultivated in Constructed Wetlands of Mexico. *Sustainability*, 13(11), 6267.
- Zitácuaro-Contreras, I., Marín-Muñiz, J. I., Zamora-Castro, S. A. (2024). La educación en México hacia la sustentabilidad: un área de oportunidad para el bienestar socio-ambiental. En Ortega, P. G., Ronquillo, B. N. R. Edit. *La educación, un camino seguro para el futuro*. 114-134. IVES.
- Zurita F., Castellanos-Hernández O.A., y Rodríguez-Sahagún A. (2011). El tratamiento de las aguas residuales municipales en las comunidades rurales de México. *Revista Mexicana de Ciencias Agrícolas*, 1(1), 139-150.

# Hydrodeoxygenation of anisole to produce value-added products: ortho-, meta-, para-cresol

Leonor Angélica Guerrero Zúñiga <sup>1</sup>, Ana Cristina Ramirez-Gallardo <sup>2</sup>, Maria Fernanda López Sánchez <sup>2</sup> and Isidoro Garcia-Cruz <sup>2,\*</sup>

<sup>1</sup> Research Management in Energy Efficiency and Biofuels. Mexican Petroleum Institute, Mexico City, Mexico.

<sup>2</sup> Research Management in Industrial Transformation. Mexican Petroleum Institute, Mexico City, Mexico.

\* Corresponding author: [igarcia@imp.mx](mailto:igarcia@imp.mx)

Received: May 9, 2025

Accepted: June 13, 2025

Published: June 18, 2025

DOI: <https://doi.org/10.56845/rebs.v7i1.451>

**Abstract:** This work presents a detailed study on the trans-methylation reaction using density functional theory (DFT), an advanced computational technique for analyzing and predicting molecular-level interactions. Trans-methylation is a crucial step in both catalytic and non-catalytic decomposition of methoxybenzene (anisole), with a special focus on processes generating free radicals and methyl-type carbocations through the cleavage of the methyl group. The study highlights that, in the presence of Brønsted-acid catalysts (such as HZSM-5), trans-methylation follows a specific mechanism involving dual electrophilic attack. This process begins with the interaction of the Brønsted acid proton with the oxygen atom in anisole, leading to carbocation substitution. This dual electrophilic attack mechanism is key as it explains how the catalyst alters reaction pathways to improve efficiency. Computational modeling of the reaction shows that the use of acidic catalysts drastically lowers the energy barriers of the investigated compounds, indicating that Brønsted acidity facilitates the reaction. In many cases, the reduction exceeds 40 kcal/mol, with the most significant decrease observed for ortho-cresol, where the energy barrier drops by approximately 60 kcal/mol. This demonstrates the significant influence of the catalyst on reaction kinetics. Both in catalytic and non-catalytic trans-methylation, there is a clear structural preference for the anisole molecule and its derivatives, such as cresols. The ortho and para positions are the most favored for substitution, especially when the substituents are oxygen-rich. This is because oxygenated substituents tend to lower energy barriers and enhance the reactivity of the aromatic ring, as seen in the decomposition of anisole into phenolic derivatives. This work demonstrates how the use of Brønsted-acid catalysts not only accelerates trans-methylation reactions but also alters the preferred reaction pathways, significantly reducing energy barriers. This opens the door to a deeper understanding and optimization of industrial processes involving the decomposition of aromatic compounds such as anisole. The production of benzene, toluene, and xylene (BTX), along with oxygenated aromatic compounds such as anisole and cresol, plays a significant role in various industrial applications, including the synthesis of polymers, resins, and fuel additives. While the manufacture of these aromatics is associated with environmental concerns—particularly emissions and toxic by-products—their contribution to sustainability can be enhanced through the adoption of greener synthesis pathways, improved catalytic efficiency, and the integration of renewable feedstocks. When aligned with circular economy principles and process intensification strategies, the production of BTX and oxygenated aromatics can support more sustainable chemical manufacturing frameworks.

**Keywords:** Hydrodeoxygenation; anisole; products; cresol

## Introduction

The large-scale production of benzene, toluene, and xylene (BTX) is essential for the national petrochemical industry. In this context, anisole is frequently used as a model compound to study the reactivity of lignin derivatives containing the methoxy functional group, given that anisole contains this as its sole functional group (Hurff & Klein, 1983). It has been observed that trans-methylation is the primary reaction in both the catalytic and non-catalytic decomposition of anisole, leading to the production of BTX compounds and phenol, as illustrated in Figure 1 (Qinglei *et al.*, 2015) (Prasomsri *et al.*, 2011) (Wang *et al.*, 2014) (Cornella *et al.*, 2013) (Mackie *et al.*, 1989).

Catalytic hydrodeoxygenation (HDO) of anisole is a critical and efficient step to upgrade raw bio-oil, converting it into high-quality transportation fuels by reducing oxygen content and increasing calorific value. However, catalytic cracking can reduce the yield of liquid fuels and increase that of gaseous fuels, leading to carbon losses and the formation of short-chain hydrocarbons (C<sub>1</sub> to C<sub>4</sub>). To produce high-performance fuels such as bio-jet fuel for aviation, it is essential to understand the HDO catalytic conversion process of biomass, which will enable better design of metallic catalysts and optimization of reaction conditions.

Given the complexity of raw bio-oil derived from biomass, the main objective of this work is to investigate the catalytic HDO reaction pathway of model compounds like anisole. First, the chemical and electronic structures of anisole and its

derivatives will be analyzed, as well as the structure of the HZSM5 zeolite-based catalyst, which has a significant impact on the conversion and selectivity of value-added products obtained from anisole degradation.

Previous studies have reported that the use of Ni supported on  $\text{TiO}_2\text{-ZrO}_2$  (with 70 mol%  $\text{TiO}_2$ ) as a catalyst enhances anisole HDO activity and selectivity toward hydrocarbons such as cyclohexane and benzene due to its improved dispersion and higher acidity. Additionally, it has been reported that bimetallic catalysts can increase anisole activity and modify its selectivity (Rios-Escobedo *et al.*, 2022) (Zhang *et al.*, 2014). Therefore, catalyst acidity is crucial, making zeolite-based catalysts an attractive alternative due to their significantly lower cost compared to metal-based catalysts such as Ni, Pd, and Ru.

This work proposes to study the reaction pathway of anisole using HDO catalysts, as shown in Figure 1. The reaction of anisole over HZSM5 zeolite-based HDO catalysts will be investigated to obtain value-added products such as cyclohexane, phenol, cyclohexene, toluene, and ortho-, meta-, and para-cresol. These products will be generated through different processes, including demethoxylation (DMO), hydrogenation (HYD), demethylation (DME), and alkylation (ALK). Alkylation will occur through the trans-methylation of the  $\text{CH}_3^+$  - group in phenol, forming the ortho-, meta-, and para-cresol isomers.

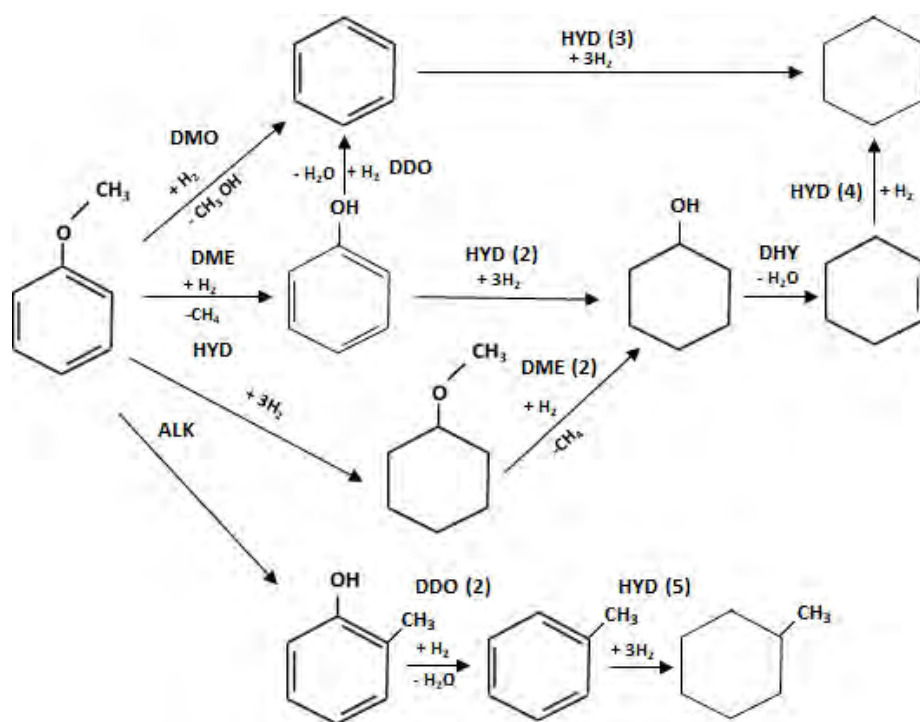


Figure 1. Reaction pathways of anisole over HDO catalysts

### Methodology for Calculations and Reaction Schemes

Figure 1 and Figure 2 present the reaction scheme for the alkylation (ALK) of anisole, specifically the trans-methylation of the  $\text{CH}_3^+$  - group at the ortho-, meta-, and para- positions of phenol, leading to the formation of ortho-, meta-, and para-cresol. The structures of anisole and its derivatives were optimized using density functional theory (DFT), employing the B3LYP functional (Lee *et al.*, 1988) and the 6-31G(2df,p) basis set (Csonka *et al.*, 2009) (Assary *et al.*, 2010).

The B3LYP functional was selected because it is a widely used and well-parametrized reference functional for thousands of organic molecules, making it a reliable choice for this type of calculation. Additionally, the 6-31G(2df,p) basis set was chosen because oxygenated molecules such as anisole, phenol, and the HZSM5 zeolite contain oxygen atoms, which require the inclusion of atomic orbitals p, d, and f to account for the polarization and diffusion necessary for accurately describing the polarity of these systems.

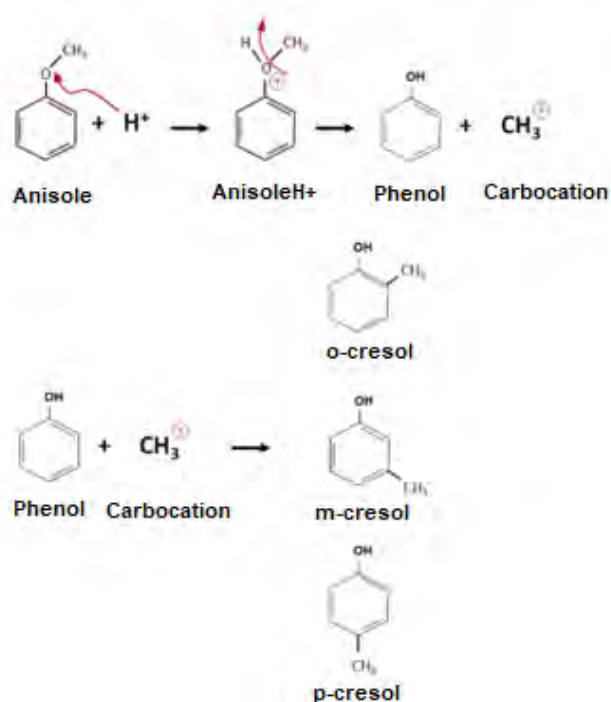


Figure 2. Reaction scheme of the methyl group ( $CH_3^+$ ) trans-methylation from anisole to phenol to form ortho-, meta-, and para-cresol

To aid in understanding the optimized structures, Figure 3 provides the atom numbering in the structures and the representative species involved in the trans-methylation reaction for phenol formation. Meanwhile, Figure 4 shows the optimized structures of anisole and its derivatives obtained via DFT, which enable the formation of ortho-, meta-, and para-cresol.

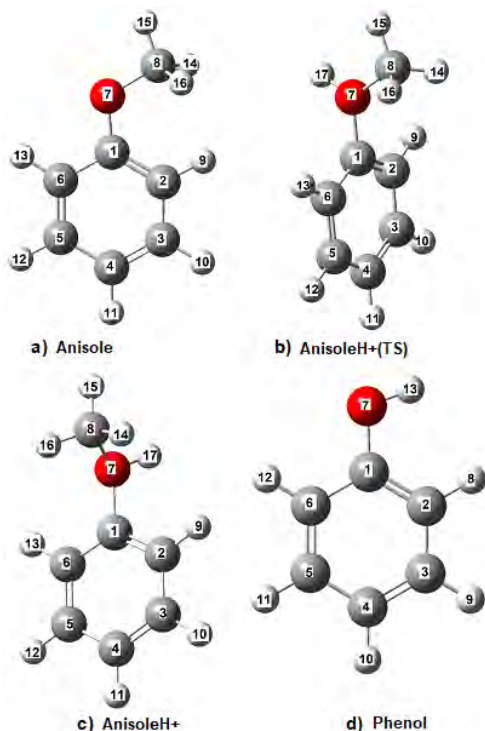


Figure 3. Numbering of the optimized geometry of the main components of the trans-methylation of anisole at the B3LYP/6-31G(2df,p) level

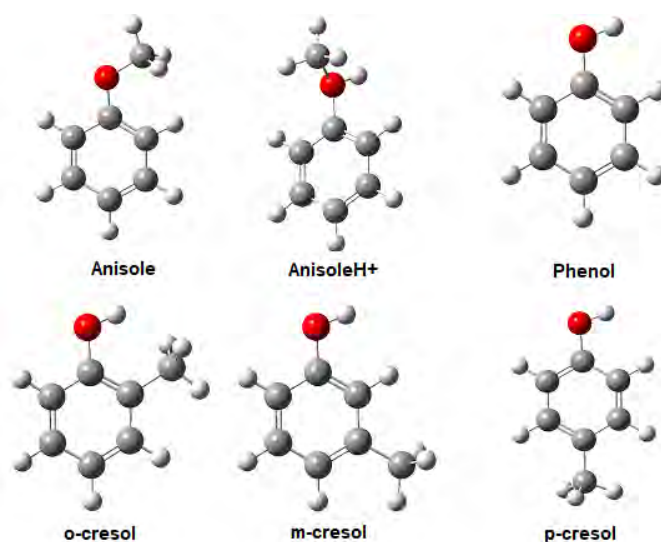


Figure 4. Optimized geometry of the main components of the trans-methylation of anisole at the B3LYP/6-31G(2df,p) level

During the optimization of anisole and its derivative structures using DFT, additional properties were calculated, including the total energy of the system, the energy of the highest occupied molecular orbital (HOMO), the energy of the lowest unoccupied molecular orbital (LUMO), and the energy gap between the HOMO and LUMO orbitals. Furthermore, Mulliken charges of all atoms in the system were determined, along with Fukui reactivity indices:

- $f(+)$  for electrophilic substitutions,
- $f(-)$  for nucleophilic substitutions,
- $f(r)$  for radical-mediated substitutions.

These calculations provide a comprehensive understanding of the electronic structure and reactivity of anisole and its derivatives, facilitating the analysis of reaction pathways for the formation of value-added products.

## Results and Discussion

The results section should include a precise description of the experimental results, a discussion of these results and their interpretation from the perspective of previous research and the hypotheses proposed. It is also necessary to mention possible future research.

The optimized structure of anisole and its derivatives obtained via DFT is shown in Figure 4. Table 1 details the bond distances and angles, while Table 2 presents the bond orders (B.O.), and Table 3 displays Mulliken electronic charges, as well as the Fukui reactivity indices calculated in this work and compared with those reported in the literature by Zhang *et al.* (2017). Finally, Figure 5 and Table 4 present the reaction barriers in kcal/mol for the trans-methylation reaction of anisole.

Table 1. Bond distance (in Å), bond angle, and dihedral angle (in °) of the optimized structures of anisole and its derivatives obtained at the B3LYP/6-31G(2df,p) level

	Anisole, A	AH(TS)	AH <sup>+</sup>	Phenol
<b>Bond distances (Å)</b>				
C <sub>1</sub> -O <sub>7</sub>	1.362	1.461	1.474	1.364
C <sub>8</sub> -O <sub>7</sub>	1.414	1.484	1.495	
C <sub>1</sub> -C <sub>2</sub>	1.397	1.381	1.381	1.396
C <sub>1</sub> -C <sub>6</sub>	1.401	1.381	1.379	1.396
<b>Bond angles (°)</b>				
C <sub>1</sub> C <sub>7</sub> C <sub>8</sub>	118.21	123.37	117.86	109.01
<b>Dihedral angles (°)</b>				
C <sub>2</sub> C <sub>1</sub> O <sub>7</sub> C <sub>8</sub>	179.98	89.81	97.82	179.91

### 1. Optimized Structure of Anisole and Its Derivatives

The optimized geometry of anisole (A) using DFT reveals that the C<sub>1</sub>-O<sub>2</sub> bond distance is 1.362 Å. In the transition state structure AH(TS), this distance increases to 1.461 Å, while in the protonated anisole AH<sup>+</sup> it is 1.474 Å, and in phenol, it is 1.364 Å. The C<sub>8</sub>-O<sub>7</sub> bond distance in anisole is 1.414 Å; in AH(TS) it increases to 1.484 Å, and in AH<sup>+</sup> it is 1.449 Å. The C<sub>1</sub>-C<sub>2</sub> bond distance in anisole is 1.397 Å, reducing to 1.381 Å in both AH(TS) and AH<sup>+</sup>, and it is 1.396 Å in phenol. On the other hand, the C<sub>1</sub>-C<sub>6</sub> bond distance in anisole is 1.401 Å; in AH(TS) it is 1.381 Å, in AH<sup>+</sup> it is 1.379 Å, and in phenol, it is 1.396 Å.

The  $C_1 - O_7 - C_8$  bond angle in anisole is  $118.21^\circ$ , while in AH(TS) it increases to  $123.37^\circ$  and in  $AH^+$  it is  $117.86^\circ$ . The dihedral angle  $C_6C_1O_7C_8$  in anisole is  $179.98^\circ$ , but in AH(TS) it significantly decreases to  $89.81^\circ$ , and in  $AH_+$  it is  $97.82^\circ$ , as detailed in Table 1. Although the bond distances and angles undergo some adjustments, no significant changes are observed in the optimized geometry of anisole and its derivatives, except for the dihedral angle. In the optimized structure of anisole, the  $CH_3O-$  group is positioned at a dihedral angle of  $C_2C_1O_7C_8$  of  $180^\circ$  in the plane of the benzene ring. In the transition state, this angle reduces to  $90^\circ$ , and in protonated anisole, it is nearly  $98^\circ$ , as shown in Table 1. The geometric optimization of anisole and its derivatives shows that the aromatic ring structure remains resonant and highly stable. The main structural changes are observed around the  $CH_3O-$  group. The  $C_8 - O_7$  distance is longer compared to the  $C_1 - O_7$  distance, which facilitates the cleavage of the  $C_8 - O_7$  bond to form the  $CH_3^+$  radical and phenol. Since the  $C_1 - O_7$  bond distance is slightly larger, this cleavage may be easier, leading to the formation of benzene and methanol. After the formation of phenol, the trans-methylation leads to the formation of ortho-, meta-, and para-cresol, as shown in Figure 2 and Figure 4.

## 2. Bond order of anisole and protonated anisole

Table 2 shows the bond order (B.O.) of anisole and its protonated version. It is observed that the  $C_1-O_7$  bond has a B.O. of 0.67, while the  $C_8-O_7$  bond has a B.O. of 0.52, both with lower values compared to the rest of the molecule. The average B.O. of the C-C bonds in anisole is 1.03, and that of the C-H bonds is 0.81. The  $C_8-H_{15}$  bond has a B.O. of 0.83, higher than the average for C-H bonds, stabilizing the resonant structure of anisole by forming a dihedral angle  $C_1-O_7-C_8-H_{15}$ . This behavior is also observed in the protonated anisole, although the B.O. of  $C_1-O_7$  and  $C_8-O_7$  are lower, indicating that the structure is less stable and more reactive, which facilitates its decomposition to form phenol.

Table 2. Mulliken bond order (B.O.) of the anisole (A) molecule and the protonated anisole ( $AH^+$ ) for the trans-methylation reaction estimated at the B3LYP/6-31G(2df,p) level

Bond	B. O. Mulliken	
	A	$AH^+$
$C_1-C_2$	1.030	0.099
$C_1-C_6$	1.032	1.024
$C_1-O_7$	0.668	0.364
$C_8-O_7$	0.515	0.333
$C_2-C_3$	1.003	1.026
$C_3-C_4$	1.030	1.012
$C_4-C_5$	1.063	1.007
$C_5-C_6$	1.032	1.012
$C_2-H_9$	0.813	0.819
$C_3-H_{10}$	0.824	0.834
$C_4-H_{11}$	0.825	0.836
$C_5-H_{12}$	0.821	0.836
$C_6-H_{13}$	0.814	0.828
$C_8-H_{14}$	0.798	0.803
$C_8-H_{15}$	0.826	0.814
$C_8-H_{16}$	0.799	0.809
$O_7-H_{17}$	-----	0.676

The  $Csp^3-O$  bond in the optimized structure of the anisole molecule, with a  $C_8-O_7$  bond distance of  $1.414 \text{ \AA}$ , is the weakest. This distance increases to  $1.484 \text{ \AA}$  in the transition state structure AH(TS) and to  $1.449 \text{ \AA}$  in the protonated anisole  $AH^+$ , indicating that it is a weak bond, making it easier for the anisole molecule to break, forming the  $CH_3^+$  cation and phenol, as shown in Figure 2 and Table 1. In this case,  $C_8$  corresponds to the  $CH_3^+$  group, and  $O_7$  is the oxygen atom of the methoxy group, suggesting that both non-catalytic and catalytic thermal decomposition of anisole preferentially begin at this site (Li *et al.*, 2014). In the case of non-catalytic decomposition of anisole, when the  $C_8-O_7$  bond in the anisole molecule breaks, a methyl radical is formed, which substitutes a hydrogen atom in a phenol molecule to produce ortho-, meta-, and para-cresol (Zhang *et al.*, 2017). It is likely that substitutions by the  $CH_3^+$  radical

preferentially occur at the ortho- and para- positions of the phenol molecule because these positions favor an electrophilic attack, according to the Fukui reactivity indices (+) (Table 3). In a previous experimental study from Assary *et al.* (2010), it was established that the formation of cresol at temperatures below 650 °C is favored during the non-catalytic decomposition of anisole. It is important to note that, since there is no stable compound or intermediate in non-catalytic trans-methylation reactions, it is likely that cresol is obtained through a one-step reaction.

Table 3. Mulliken charges and Fukui reactivity indices for the atoms of anisole and its derivatives for electrophilic attack (Fukui(-)), calculated at the B3LYP/6-31G(2df,p) level and compared with the literature values.

Anisole/Atom	Mulliken C. This work	Mulliken C. (Assary <i>et al.</i> , 2010)	Fukui Index f(-) (Assary <i>et al.</i> , 2010)
A			
C <sub>1</sub>	0.410	0.299	0.075
C <sub>2</sub>	-0.257	-0.064	0.086
C <sub>3</sub>	-0.089	-0.083	0.061
C <sub>4</sub>	-0.127	-0.063	0.125
C <sub>5</sub>	-0.085	-0.097	0.071
C <sub>6</sub>	-0.194	-0.133	0.072
O <sub>7</sub>	-0.264	-0.438	0.129
C <sub>8</sub>	-0.245	0.008	0.035
H <sub>9</sub>	0.094	0.074	0.046
H <sub>10</sub>	0.093	0.077	0.044
H <sub>11</sub>	0.090	0.088	0.057
H <sub>12</sub>	0.094	0.081	0.046
H <sub>13</sub>	0.099	0.076	0.040
H <sub>14</sub>	0.123	0.087	0.037
H <sub>15</sub>	0.134	0.102	0.038
H <sub>16</sub>	0.123	0.086	0.036

AH <sub>n</sub>	Mulliken C. This work	Mulliken C. (Assary <i>et al.</i> , 2010)	Fukui Index f(-) (Assary <i>et al.</i> , 2010)	Fukui Index f(-) (Assary <i>et al.</i> , 2010)
C <sub>1</sub>	0.315	0.216	0.058	0.048
C <sub>2</sub>	-0.212	-0.099	0.038	0.134
C <sub>3</sub>	-0.076	-0.048	0.024	0.128
C <sub>4</sub>	-0.090	-0.046	0.085	0.059
C <sub>5</sub>	-0.081	-0.049	0.025	0.120
C <sub>6</sub>	-0.175	-0.069	0.046	0.142
O <sub>7</sub>	-0.236	-0.370	-0.057	0.017
C <sub>8</sub>	-0.278	0.006	0.138	0.017
H <sub>9</sub>	0.147	0.116	0.060	0.056
H <sub>10</sub>	0.163	0.126	0.070	0.056
H <sub>11</sub>	0.161	0.127	0.050	0.045
H <sub>12</sub>	0.164	0.128	0.071	0.055
H <sub>13</sub>	0.162	0.130	0.070	0.058
H <sub>14</sub>	0.210	0.151	0.050	0.017
H <sub>15</sub>	0.226	0.166	0.063	0.046
H <sub>16</sub>	0.217	0.161	0.050	0.016
H <sub>17</sub>	0.382	0.354	0.140	0.024

Continuation Table 3. Mulliken charges and Fukui reactivity indices for the atoms of anisole and its derivatives for electrophilic attack (Fukui(-)), calculated at the B3LYP/6-31G(2df,p) level and compared with the literature values.

Phenol	Mulliken C. This work	Mulliken C. (Assary <i>et al.</i> , 2010)	Fukui Index f(0) (Assary <i>et al.</i> , 2010)	Fukui Index f(-) (Assary <i>et al.</i> , 2010)
C <sub>1</sub>	0.410	0.283	0.073	0.089
C <sub>2</sub>	-0.251	-0.074	0.105	0.089
C <sub>3</sub>	-0.077	-0.144	0.095	0.068
C <sub>4</sub>	-0.130	-0.072	0.102	0.136
C <sub>5</sub>	-0.082	-0.119	0.099	0.073
C <sub>6</sub>	-0.184	-0.091	0.100	0.083
O <sub>7</sub>	-0.444	-0.440	0.103	0.152
H <sub>8</sub>	0.081	0.057	0.057	0.049
H <sub>9</sub>	0.095	0.059	0.055	0.061
H <sub>10</sub>	0.092	0.071	0.056	0.048
H <sub>11</sub>	0.096	0.054	0.056	0.050
H <sub>12</sub>	0.102	0.058	0.055	0.048
H <sub>13</sub>	0.296	0.257	0.044	0.055

### 3. Reaction barrier of anisole and its derivatives

Figure 5 and Table 4 show the reaction barrier in kcal/mol for the formation of ortho-, meta-, and para-cresol from the HDO of anisole. As can be seen in Figure 5, the critical step is the large reaction barrier of over 170 kcal/mol to reach the transition state AH(TS). This reaction barrier decreases to 7 kcal/mol to form a highly reactive and unstable species, protonated anisole (AH<sup>+</sup>). This unstable species is highly reactive and favors the formation of phenol through the elimination of the CH<sub>3</sub><sup>+</sup> group. After the formation of protonated anisole, the reaction barrier decreases to -87 kcal/mol to form phenol, a very stable molecule. This phenol can then react with the CH<sub>3</sub><sup>+</sup> group at the ortho-, meta-, and para-positions via the trans-methylation of the CH<sub>3</sub><sup>+</sup> group. The trans-methylation of CH<sub>3</sub><sup>+</sup> allows the formation of the respective cresol, with lower reaction barriers of -97 kcal/mol and -98 kcal/mol for ortho- and meta-cresol, and -100 kcal/mol for para-cresol. This small variation in the reaction barrier of ~3 kcal/mol for the formation of ortho-, meta-, and para-cresol could justify the earlier statement by the group of Zhang *et al.* (2016), that the formation of cresol can occur in a single step.

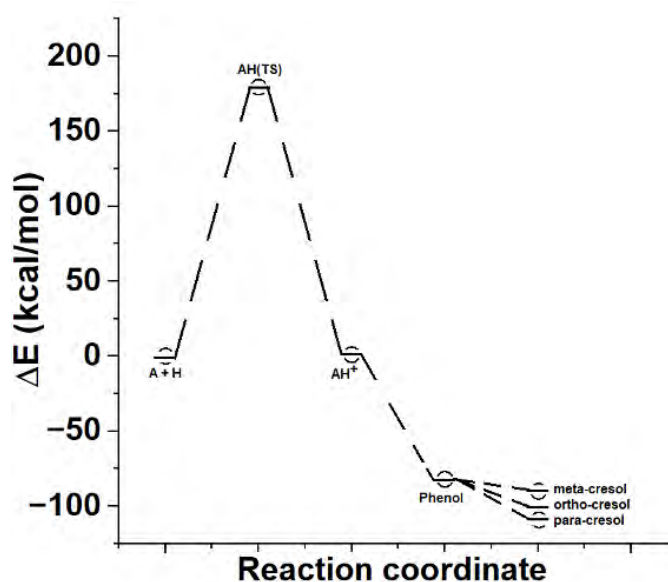


Figure 5. Energy barrier in kcal/mol for anisole to form phenol, ortho-, meta-, and para-cresol obtained with B3LYP/6-31G(2df,p)

Table 4. Energy barriers in kcal/mol for the HDO of anisole and the species involved in the reaction

Molecules/Species	Ezpc	$\Delta H$ Enthalpy	$\Delta G$ Free energy
A+H	0.00	0.00	0.00
AH	178.95	179.38	177.77
AH <sup>+</sup>	0.93	0.94	0.44
Phenol	-80.96	-82.06	-71.61
o-Cresol	-100.55	-99.20	-110.64
m-Cresol	-100.22	-98.99	-109.64
p-Cresol	-100.68	-99.47	-110.06

On the other hand, in the case of the catalytic decomposition of anisole over Brønsted acid sites of the HZSM5 zeolite, it has been established that the trans-methylation reaction is induced by a proton dissociated from the acidic site (-AlOH) and causes an electrophilic attack by one or more carbocations on anisole (Haw *et al.*, 1989) (Richardson *et al.*, 1990) (Munson *et al.*, 1993) (Xu *et al.*, 1994).

These studies state that the trans-methylation mechanism proceeds through carbocation transfers in the case of catalytic decomposition of anisole, as shown in Figure 2 and Figure 4.

The catalytic process of trans-methylation can be divided into two stages: i) the first consists of the cleavage or splitting of the methyl group  $\text{CH}_3^+$  in the anisole molecule; the proton dissociated from the acid site of the catalyst causes an initial electrophilic attack on the oxygen atom of the anisole molecule, as shown in Figure 2 and Figure 4, and a methyl carbocation  $\text{CH}_3^+$  is released. This  $\text{CH}_3^+$  promotes a second electrophilic attack (Figure 2), and it is likely that this  $\text{CH}_3^+$  group replaces a hydrogen atom at the ortho-, meta-, and para- positions of phenol, as shown in Figure 2 and Figure 4. The displaced free proton simultaneously interacts with the catalyst to regenerate the Brønsted acid site, thereby maintaining catalytic activity during the reaction. The transition-state species typically exist for a short time; however, the  $\text{CH}_3^+$  bound to the active site during the trans-methylation process is a relatively stable structure (Figure 2), and carbocation substitution reactions via an electrophilic attack (Table 3) are favored as separate steps in catalytic trans-methylation. The mechanism in Figure 2 shows that the use of a Brønsted acid-type catalyst (the HZSM5 zeolite) replaces the one-step direct transfer reaction of  $\text{CH}_3^+$  observed for the non-catalytic reaction with a two-step process (Zhu *et al.*, 2010). The HZSM5-Anisole reaction mechanism also demonstrates the constant maintenance of acid sites in the catalyst by proton recovery throughout the reaction.

It is important to note that in both the catalytic and non-catalytic decomposition of anisole, the methyl group is transferred not only to phenol but also to other compounds such as benzene and toluene present in the reaction medium (Zhang *et al.*, 2016). All trans-methylation processes start from the cleavage of the methyl group  $\text{CH}_3^+$  from anisole.

#### 4. HZSM5 Zeolite and its Interaction with Anisole

The Figure 6 shows the structure of the HZSM5 zeolite with four tetrahedral sites (4T). Structure A is the innermost ring of the HZSM5 zeolite structure with a Si/Al ratio of 30%, and it is the one modeled in this work. Structure B and Structure C represent the same zeolite, but with Si/Al ratios of 50% and 100%, respectively.

The geometry optimization result of the zeolite HZSM5 ring shows that the Mulliken atomic charges of the acidic hydrogens bonded to the O linked to an Al atom in a tetrahedral site and to a Si atom in the HZSM5 zeolite ring are very acidic, as shown in Table 5. The higher the charge on the hydrogen, the more acidic its character. In this work, the hydrogen atoms H(39), H(40), H(41), and H(42) in the zeolite HZSM5 ring structure are the most acidic hydrogens, which stabilize the negative charge of the 4T sites of the -AlOH anion, with H(42) being the most acidic hydrogen among all four tetrahedral sites with a charge of 0.368, followed by H<sub>40</sub> with 0.359, H<sub>41</sub> with 0.351, and finally H<sub>39</sub> with 0.345, as

seen in Table 5 and Figure 7. The most acidic tetrahedral site is where the anisole can be more easily activated in its interaction with the HZSM5 zeolite, and when the total HZSM5-zeolite-anisole interaction is reached, the protonated anisole or  $AH_+$  is formed, favoring the formation of phenol and benzene.



Figure 6. Models of HZSM5-type zeolites: A) Zeolite ring with four tetrahedral centers (4T); B) HZSM5 zeolite structure with a 50% ratio; C) HZSM5 zeolite structure with a 100% ratio. The O atom is colored red, the Si atom is gray, the Al atom is pink, and the H atom is white.

Table 5 Mulliken charges of the acidic hydrogens in the HZSM5 zeolite ring obtained at the B3LYP/6-31G(2df,p) level.

Atom/H Position in the Ring	Mulliken charge
H(39)	0.345
H(40)	0.359
H(41)	0.351
H(42)	0.368

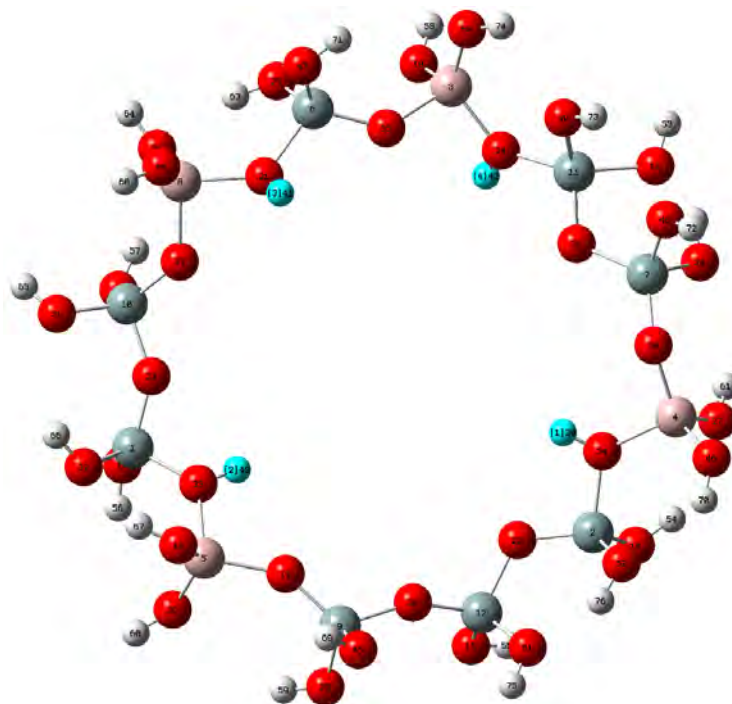


Figure 7. Structure of the HZSM5 zeolite ring optimized at the B3LYP/6-31G(2df,p) level. The atoms in light blue are the H atoms that stabilize the tetrahedral sites of  $-AlOH$

## Conclusions

The results obtained with DFT indicate that the trans-methylation reaction is a crucial step in both the non-catalytic and catalytic decomposition of anisole. The cleavage of the C<sub>8</sub>-O<sub>7</sub> bond leads to the formation of the CH<sub>3</sub><sup>+</sup> radical. In catalytic trans-methylation, the reactants interact with the Brønsted acid sites present in the HZSM5-based catalyst. This process is initiated by the electrophilic attack of the Brønsted acid proton on the oxygen atom of the anisole, followed by the substitution of the hydrogen with CH<sub>3</sub><sup>+</sup>.

In this work, a dual electrophilic attack mechanism for catalytic trans-methylation is proposed. The reaction modeling, based on the proposed mechanism, shows that a catalyst with higher Brønsted acidity can significantly reduce the energy barrier for all the compounds investigated, due to changes in the reaction pathways. Most of the energy barriers for the evaluated trans-methylation reactions decrease by approximately 40 kcal/mol when considering the catalytic effect, with the greatest decrease observed in the case of ortho-cresol (around 60 kcal/mol).

Furthermore, both non-catalytic and catalytic trans-methylation of anisole exhibit a preference for the formation of phenol, with most of the species involved showing a preference for the para-phenol position, depending on the substituents. Non-catalytic transmethylation to oxygen-rich substituted compounds generally presents lower energy barriers. In the catalytic decomposition of anisole, the presence of oxygen-rich substituents also enhances the reactivity of the ring, especially for phenolic compounds at the para- position. The lowest energy barrier was observed in the case of trans-methylation to the para- position of phenol, with the barrier to form para-cresol being approximately 102 kcal/mol.

**Acknowledgments and Funding:** The authors extend their sincere appreciation to the Mexican Petroleum Institute (IMP) for its financial support through research grant D.62026. The computational resources fundamental to this work were generously provided by the National Supercomputing Center at IPICYT (Potosino Institute of Scientific and Technological Research), under project allocation TKII-E-0424-I-170424-26/PR-33: *Mechanistic modeling of molecular disintegration in mixtures of unconventional feeds in FCC units*. The authors gratefully acknowledge the valuable infrastructure and expert technical assistance offered by the Supercomputing Center team, which played a pivotal role in the successful execution of this research.

**Declaration of competing interest:** The authors declare that they have no financial or personal conflicts of interest that could have influenced the results or interpretation presented in this manuscript. All contributions to this work were conducted with full scientific independence and integrity.

**Author contributions:** G. C.-I. and R. G.-A. C. contributed equally to the conceptual design of the study, performed the computational analyses, interpreted the data, and were primarily responsible for drafting and revising the manuscript. G. Z.-L. A. and L. S.-M. F. were responsible for providing key experimental materials, coordinating laboratory operations, designing the methodology for data acquisition, and supervising the overall research process. All authors reviewed and approved the final version of the manuscript and agree to be accountable for all aspects of the work.

## References

- Assary, R. S., Redfern, P. C., Hammond, J. R., Greeley, J., & Curtiss, L. A. (2010). Computational Studies of the Thermochemistry for Conversion of Glucose to Levulinic Acid. *The Journal of Physical Chemistry B*, 9002-9009. <https://doi.org/10.1021/jp101418f>
- Cornella, Cornella, J., Gómez-Bengoa, E., & Martin, R. (2013). Combined Experimental and Theoretical Study on the Reductive Cleavage of Inert C-O Bonds with Silanes: Ruling out a Classical Ni(0)/Ni(II) Catalytic Couple and Evidence for Ni(I) Intermediates. *Journal of the American Chemical Society*, 1997-2009. <https://doi.org/10.1021/ja311940s>
- Csonka, G. I., French, A. D., Johnson, G. P., & Stortz, C. (2009). Evaluation of Density Functionals and Basis Sets for Carbohydrates. *Journal of Chemical Theory and Computation*, 679-692. <https://doi.org/10.1021/ct8004479>
- Haw, J. F., Richardson, B. R., Oshiro, I. S., Lazo, N. D., & Speed, J. A. (1989). Reactions of propene on zeolite HY catalyst studied by in situ variable temperature solid-state nuclear magnetic resonance spectroscopy. *Journal of the American Chemical Society*, 2052-2058. <https://doi.org/10.1021/ja00188a016>
- Hurff, S. J., & Klein, M. T. (1983). Reaction pathway analysis of thermal and catalytic lignin fragmentation by use of model compounds. *Industrial & Engineering Chemistry Fundamentals*, 426-430. <https://doi.org/10.1021/i100012a012>
- Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 785. <https://doi.org/doi.org/10.1103/PhysRevB.37.785>
- Li, G., Li, L., Jin, L., Tang, Z., Fan, H., & Hu, H. (2014). Experimental and Theoretical Study on the Pyrolysis Mechanism of Three Coal-Based Model Compounds. *Energy & Fuels*, 980-986. <https://doi.org/10.1021/ef402273t>

- Mackie, J., Doolan, K., & Nelson, P. (1989). Kinetics of the thermal decomposition of methoxybenzene (anisole). *The Journal of Physical Chemistry*, 664-670. <https://doi.org/10.1021/j100339a033>
- Munson, E. J., Xu, T., & Haw, J. F. (1993). In situ nuclear magnetic resonance study of allyl alcohol conversion on zeolites: evidence for an allyl cation intermediate. *Journal of the Chemical Society, Chemical Communications*, 75-76. <https://doi.org/10.1039/C39930000075>
- Prasomsri, T., To, A. T., Crossley, S., Alvarez, W. E., & Resasco, D. E. (2011). Catalytic conversion of anisole over HY and HZSM-5 zeolites in the presence of different hydrocarbon mixtures. *Applied Catalysis B: Environmental*, 204-211. <https://doi.org/10.1016/j.apcatb.2011.05.026>
- Qinglei, M., Honglei, F., Huizhen, L., Huacong, Z., Zhenhong, H., Zhiwei, J., . . . Buxing, H. (2015). Efficient Transformation of Anisole into Methylated Phenols over High-Silica HY Zeolites under Mild Conditions. *ChemCatChem*, 2831-2835. <https://doi.org/10.1002/cctc.201500479>
- Richardson, B. R., Lazo, N. D., Schettler, P. D., White, J. L., & Haw, J. F. (1990). Reactions of butadiene in zeolite catalysts by in situ variable-temperature solid-state nuclear magnetic resonance spectrometry. *Journal of the American Chemical Society*, 2886-2891. <https://doi.org/10.1021/ja00164a007>
- Ríos-Escobedo, R., Ortiz-Santos, E., Colín-Luna, J., Díaz de León, J., del Angel, P., Escobar, J., & de los Reyes, J. (2022). Anisole Hydrodeoxygenation: A Comparative Study of Ni/TiO<sub>2</sub>-ZrO<sub>2</sub> and Commercial TiO<sub>2</sub> Supported Ni and NiRu Catalysts. *Topics in Catalysis*, 1448-1461. <https://doi.org/10.1007/s11244-022-01662-x>
- Wang, K., Dong, X., Chen, Z., He, Y., Xu, Y., & Liu, Z. (2014). Highly selective synthesis of para-cresol by conversion of anisole on ZSM-5 zeolites. *Microporous and Mesoporous Materials*, 61-65. <https://doi.org/10.1016/j.micromeso.2013.11.007>
- Xu, T., Zhang, J., Munson, E. J., & Haw, J. F. (1994). A report of a persistent allyl cation on H-ZSM-5 zeolite was due to propanal. *Journal of the Chemical Society, Chemical Communications*, 2733-2735. <https://doi.org/10.1039/C39940002733>
- Zhang, J., Fidalgo, B., Shen, D., Xiao, R., & Gu, S. (2016). Mechanism of transmethylation in anisole decomposition over HZSM-5: Experimental study. *Journal of Analytical and Applied Pyrolysis*, 323-331. <https://doi.org/10.1016/j.jaap.2016.09.009>
- Zhang, J., Fidalgo, B., Kolios, A., Shen, D., & Gu, S. (2017). The mechanism of transmethylation in anisole decomposition over Bronsted acid sites: density functional theory (DFT) study. *Sustainable Energy Fuels*, 1788-1794. <https://doi.org/10.1039/C7SE00280G>
- Zhang, Zhang, X., Long, J., Kong, W., Zhang, Q., Chen, L., . . . Li, Y. (2014). Catalytic Upgrading of Bio-oil over Ni-Based Catalysts Supported on Mixed Oxides. *Energy & Fuels*, 2562-2570. <https://doi.org/10.1021/ef402421j>
- Zhu, X., Mallinson, R. G., & Resasco, D. E. (2010). Role of transalkylation reactions in the conversion of anisole over HZSM-5. *Applied Catalysis A: General*, 172-181. <https://doi.org/10.1016/j.apcata.2010.03.018>