



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

## **Cooperation Agreement**

between

### **Karlsruhe Institute of Technology**

Kaiserstraße 12, 76131 Karlsruhe, Germany

Institute of Catalysis Research and Technology (IKFT)

Engler-Bunte-Institute (EBI)

- hereinafter referred to as "KIT" -

and

### **Universidade Federal de Uberlândia**

Av. João Naves de Ávila 2121, Bloco 3P, Campus Santa Mônica, Uberlândia/MG, Brazil, CEP 38408-144

Faculty of Chemical Engineering

- hereinafter referred to as "UFU" -

- hereinafter referred to separately and jointly as "Partner" and "Partners", respectively -



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

### **Article 1 – Subject of the Agreement**

The subjects of the present Agreement shall be the research cooperation of the Partners in the field of catalysis preparation, characterization, testing and process development to improve the conversion of renewable carbon carriers.

The Partners agree to cooperate under this joint project according to the provisions outlined below.

### **Article 2 – Execution of the Work**

- 2.1 The Partners shall be obliged to execute intercoordinated partial tasks. The type and scope of the cooperation shall result from the work plans, inclusive of its updated versions, enclosed in Annex 1.
- 2.2 The Partners shall inform each other regularly and comprehensively in particular by the communication of the individual work results and work progress, by the exchange of intermediate and final reports, as well as by the exchange of information at joint project meetings.
- 2.3 Each Partner shall appoint a contact person responsible for his share of the work (with address, phone number, fax number, and e-mail address).
- 2.4 In case it turns out during the work that deadlines cannot be observed, the other Partner shall be informed immediately.
- 2.5 As for the rest, each Partner shall be responsible for the execution of the research and development work taken over by him.

### **Article 3 – Non-contractual Intellectual Property**

- 3.1 Non-contractual intellectual property shall be all project-related findings of the institute involved in the project and existing at the respective Partner at the beginning of this Agreement, in particular, know-how, inventions, property rights, copyrights, and computer programs.



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

- 3.2 Each Partner shall remain the owner of his non-contractual intellectual property.
- 3.3 Each Partner shall grant to the other Partner a cost-free, non-exclusive, non-transferable, and non-sublicensable right of use of his non-contractual intellectual property, which shall be limited to the duration and purposes of the project, provided that this is required for the execution of the project and does not conflict with any rights of third parties.
- 3.4 For purposes outside of and upon the termination of this Agreement, each Partner shall agree to grant to the other Partner a non-exclusive right of use of his non-contractual intellectual property at conditions customary on the market, provided that this is required for the use of his own work results and provided that the Partner can freely dispose of this right at the time it is granted. Prior to use, the Partners shall agree on the details in a separate agreement in writing.
- 3.5 The Partners shall inform each other about conflicting rights of third parties, as soon as they obtain knowledge thereof.

#### **Article 4 – Work Results, Property Rights, Rights of Use**

- 4.1 Work results shall be all results, inclusive of drafted reports and documents, which are developed by the Partners while executing their work under the joint project, in particular, know-how, inventions, property rights, copyrights, and computer programs.
- 4.2 Work results developed by staff members of one Partner exclusively shall become the property of this Partner.
- 4.3 Work results developed by staff members of both Partners shall become joint property of these Partners. The Partners shall agree on the application for, maintenance, or defense of patents as well as on the sharing of costs and the exploitation of joint inventions.

Prior to use in each individual case, the details shall be agreed upon in a separate agreement by the Partners at conditions customary on the market.

As long as no such separate agreement has been concluded, both Partners involved in the respective invention shall have the right to use the invention and to grant non-exclusive, non-



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

transferable, and temporarily and spatially unlimited licenses to third parties. Copyrights shall be subject to an analog proceeding.

- 4.4 Each Partner shall inform the other Partner about inventions resulting from the execution of this Agreement within a period of one month upon the application for a property right.
- 4.5 If one Partner refrains from filing an application and/or maintaining the share in an intellectual property right to which he is entitled according to Article 4.3, he will offer this intellectual property right or his share in it or the respective application to the other Partner for assignment at conditions customary on the market. In the individual case, the details of assignment shall be agreed upon by the Partners in a separate agreement.
- 4.6 Each Partner shall pay the employee invention compensations due to his staff members, unless the property right has been assigned according to Article 4.5.
- 4.7 Each Partner acknowledges that acts of use of information and objects received from the other Partner shall not constitute a right of prior use according to Article 12 of the German Patent Act (PatG).
- 4.8 The Partners shall grant to each other a non-exclusive, non-transferable, and cost-free right of use of the work results obtained in connection with the execution of the project for the purposes and term of the project exclusively.
- 4.9 For purposes outside and upon termination of this Agreement, each Partner shall agree to grant to the other Partner at the latter's request rights of use of the work results obtained in connection with the execution of this Agreement at conditions customary on the market, provided that this is necessary for the use of the own work results by the respective Partner and provided that this request is made within a period of one year upon the end of the project. Details shall be agreed upon separately and in writing by the Partners at an appropriate time prior to use.
- 4.10 Irrespective hereof, both Partners and their employees shall be granted a non-exclusive, non-transferable, sub-licensable, cost-free, and temporarily and spatially unlimited right of use of the work results for non-commercial purposes of research and education.



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

#### **Article 5 – Funding**

Each Partner shall bear the costs incurred by him in connection with the execution of this Agreement.

#### **Article 6 – Other Cooperation/External R&D Services**

- 6.1 If one Partner cooperates with a third party under this Agreement, he shall ensure that the other Partner is granted at least the same rights in the results of this third party as those he would have, if the results would have been developed by the Partner himself.
- 6.2 Prior to awarding contracts on R&D work under this Agreement, the other Partner shall be informed in writing about this planned awarding of contracts. Article 6.1 shall apply accordingly to the results of R&D contracts.
- 6.3 In case a Partner wishes to award a contract for the execution of his work under this Agreement, he shall be responsible and ensure in particular that any information disclosed to the contractor shall be treated confidentially by the latter according to Article 7 of this Agreement.

#### **Article 7 – Confidentiality, Publication**

- 7.1 Each Partner shall not disclose to third parties any information and objects received from the other Partner and designated confidential for a period of up to three years upon the termination of or withdrawal from this Agreement.
- 7.2 The obligation of confidentiality according to Article 7.1 shall not apply to such information or objects for which it can be proved that they
  - belong to the public domain through publications or the like, or
  - fall into the public domain without the fault of the receiving Partner, or
  - were disclosed to a Partner by a third party without the obligation of confidentiality, or
  - were already known to the receiving Partner prior to the disclosure by the other Partner, or



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

- have been developed by staff of the receiving Partner, who had no access to the information disclosed, or
  - have to be disclosed as a result of a legal obligation, court order, or order of an authority.
- 7.3 The Partners shall take the usual and reasonable measures to make their employees keep such information and objects confidential according to the present provisions.
- 7.4 Each Partner shall have the right to publish his own work results. When doing so, appropriate reference shall be made to the project. The Partners shall be obliged to inform the other Partner in advance about the intended publication.
- 7.5 Publications containing confidential information of the other Partner shall require the prior approval of this Partner, which must not be unreasonably refused. In case the respective Partner does not object to the publication submitted to him within a period of four weeks upon receipt, approval shall be deemed to have been granted.

Approval shall not be required, if a Partner, in fulfilling his legal obligation to publish research results, publishes basic scientific statements or knowledge only, which do not represent any business secrets of the respective Partner.

In case of doctoral or post-doctoral lecture qualification projects, the Partner having the right of approval shall observe the legal obligations and justified interests of the doctoral student or post-doctoral lecture qualification candidate as well as of the Partner supervising the student or candidate.

#### **Article 8 – Duration, Termination**

- 8.1 This Agreement shall enter into force after it has been signed by both Partners retroactively on 1<sup>st</sup> of January 2024 and shall have a duration of 3 years, unless it is terminated before this date or completed in another way.
- 8.2 The Partners shall have the right to terminate this Agreement for an important reason only. An important reason in particular shall be the situation that the results show that the objective of



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

the project cannot be reached at all or can be reached with an unreasonable expenditure only. Termination of this Agreement shall be communicated in writing to the other Partner.

- 8.3 The terminating Partner shall set up a final report and return at request any documents, documentations, data carriers, and objects received from the other Partner.

#### **Article 9 – Liability**

- 9.1 The Partners shall properly execute, to the best of their knowledge and taking into account the current state of the art, all work taken over by them under the joint project. The Partners shall not assume any warranty for a concrete research and development result being achieved, for the work results being suited for commercial exploitation and/or technical application, and for the absence of rights of third parties. As soon as such property rights become known to one Partner, however, he shall inform the other Partner accordingly.

- 9.2 The Partners shall mutually waive any claims for damage, except in case of intent or gross negligence. In case of gross negligence, liability for consequential damage shall be excluded.

Notwithstanding Article 426 of the Civil Code (BGB), the Partners agree that in case of claims of third parties, they shall only be liable according to their share in the fault, and they shall be obliged to indemnify the other Partner from any further claims.

- 9.3 The exclusions and limitations of liability shall not apply to claims according to the Product Liability Act (Produkthaftungsgesetz) based on fraudulent behavior or claims based on the liability for guaranteed characteristics and for the injury of life, body, or health.

#### **Article 10 – Concluding Provisions**

- 10.1 Should a provision of this Agreement be or become invalid, this shall not affect the validity of the remaining provisions of this Agreement or the Agreement in its entirety. The said provision shall be replaced retroactively by a new legally valid provision, the result of which shall reflect as much as possible the invalid provision which it will replace.



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

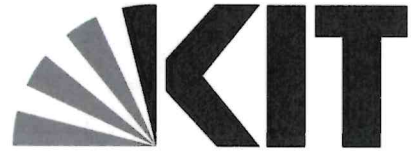
- 10.2 Any modifications and amendments of this Agreement shall be in writing to be effective. This requirement of written form shall be waived in writing only.
- 10.3 The Partners shall not have the right to make legally binding declarations with effect for the other Partner or for the Partners together or to enter obligations without the other Partner's prior express approval in writing.
- 10.4 Rights, except for property rights or shares in them, and obligations arising from this Agreement shall not be assignable without the prior approval in writing by the other Partner.
- 10.5 The present Agreement shall replace any and all oral or written agreements made by the Partners with respect to the project before this Agreement was signed.
- 10.6 The Partners shall endeavor to find a consensual solution to any dispute and doubt that may arise while implementing and interpreting this agreement. Should this not be possible, the Partners agree in the first instance to discuss and consider referring the dispute to the ICC Mediation Rules. However, this shall not prevent any Partner from commencing litigation according to Article 10.7 below.
- 10.7 Eventual doubts and disputes will be solved by the jurisdiction and according to the applicable law where the respective defendant is seated. As for claims against the UFU, the Forum of Federal Court, Judicial Section of Uberlândia, will be in charge of the cases. As for claims against the KIT, the competent courts in Karlsruhe will be in charge of the cases.
- 10.8 The UFU shall publish an abridged version of the terms of this Agreement and its amendments in the federal official gazette *Diário Oficial da União* by the fifth (5th) work day of the month following the signature of this document.
- 10.9 The following annex shall be part of this Agreement:

- Annex 1: Work Plans





**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

**Karlsruhe Institute of Technology**

Karlsruhe, 17.04.2024 2024

P.A. d. Gede. - UG/Inst. - P.A. Esler *Esler*



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

**Universidade Federal de Uberlândia**

Uberlândia; March, 25<sup>th</sup> 2024

**VALDER STEFFEN  
JUNIOR:778043418**

**49**

Assinado digitalmente por VALDER STEFFEN  
JUNIOR:77804341848  
ND: C=BR, O=ICP-Brasil, OU=Secretaria da Receita Federal do Brasil - RFB, OU=RFB e-CPF A3, OU=VALID, OU=AR  
RENOVA CERTIFICACAO DIGITAL, OU=Presencial, OU=22977901000170, CN=VALDER STEFFEN  
JUNIOR:77804341848  
Razão: Eu estou aprovando este documento com minha assinatura de vinculação legal  
Localização:  
Data: 2024.04.04 14:11:32-03'00'  
Foxit PDF Reader Versão: 12.1.2

Prof. Dr. Valder Steffen Júnior

Rector

Universidade Federal de Uberlândia



Documento assinado digitalmente  
**RICARDO REIS SOARES**  
Data: 25/03/2024 15:43:26-0300  
Verifique em <https://validar.iti.gov.br>

Prof. Dr. Ricardo Reis Soares

Faculdade de Engenharia Química

Universidade Federal de Uberlândia

Witness:



Documento assinado digitalmente  
**WALDENOR BARROS MORAES FILHO**  
Data: 11/04/2024 13:49:10-0300  
Verifique em <https://validar.iti.gov.br>

Prof. Dr. Waldenor Barros Moraes Filho

International Affairs Director

Universidade Federal de Uberlândia



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

**Annex 1: Work Plans**

**Responsible partners:**

*a. Caroline Carriel Schmitt*

Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology

Hermann-von-Helmholtz-Platz, 76344 Eggenstein-Leopoldshafen, Baden-Württemberg, Germany

Phone number: +49 721608-26255

Email: caroline.schmitt@partner.kit.edu

*b. Klaus Raffelt*

Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology

Hermann-von-Helmholtz-Platz, 76344 Eggenstein-Leopoldshafen, Baden-Württemberg, Germany

Phone number: +49 721608-26507

Email: klaus.raffelt@kit.edu

*c. Ricardo Reis Soares*

Universidade Federal de Uberlândia - UFU

Faculdade de Engenharia Química - FEQU

Catalytic and Thermochemical Processes Research Group (GPCATT)

Av. João Naves de Ávila 2121, Bloco 1K

Campus Santa Mônica – Uberlândia/MG, Brazil

CEP 38408-100

Email: rrsoares@ufu.br



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

## **Project 1**

### **1. Project title**

Evaluation of thermochemical and chemo-catalytic conversion routes for fuels and chemicals

### **2. Partners' activities**

The project will combine the strengths of Universidade Federal de Uberlândia, in terms of gas-phase hydrodeoxygenation, niobia-based catalysts design and characterization with the strengths of the Institute of Catalysis Research and Technology in terms of fast pyrolysis, catalyst preparation and characterization, catalytic hydrotreatment and hydrothermal liquefaction.

a. Universidade Federal de Uberlândia (UFU) - Catalytic and Thermochemical Processes Research Group (GPCATT)

GPCATT/UFU will carry out the niobia-based catalysts preparation, characterization (FRX, DRX, TPR, H<sub>2</sub>-/CO-/NH<sub>3</sub>-TPD, TPO), and the catalytic evaluation under gas-phase hydrodeoxygenation (HDO) of bio-oil-derived molecules, such as guaiacol, syringol, and levoglucosan.

GPCATT/UFU will also investigate the best reaction condition by thermodynamics analysis.

b. Institute of Catalysis Research and Technology (IKFT)

The fast pyrolysis of selected biomass, batch and continuous catalytic hydrotreatment reactions in liquid phase will be conducted at IKFT. The feedstocks and products will be deeply characterized by the analytical techniques available at the institute.

### **4. Goals**

The goal of the project is to investigate the vapor-phase and the liquid-phase catalytic HDO of pyrolysis- and/or HTL-derived bio-oil or its representative molecules such as syringol (and/or isoeugenol and/or levoglucosan) and its thermodynamics analysis as well. It aims the catalyst design, characterization, and HDO evaluation under different reaction conditions towards fuels and chemicals.



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

## 5. Work packages

### **WP1: Analysis of thermodynamics (UFU and IKFT)**

Thermodynamic analysis comprising the chemical equilibrium of the gas-phase HDO (UFU - Task 1.1) and liquid-phase HDO (IKFT – Task 1.2). It will be conducted by using UniSim Design R400 (UFU). Both the equilibrium constants method and the minimization of the Gibbs free energy method will be applied.

### **WP2: Catalyst preparation – powder and pellets (UFU and IKFT)**

Pt, Ru and Ni-Fe supported on Nb<sub>2</sub>O<sub>5</sub> in powder will be prepared by different methods. Ni-Fe supported catalysts on SiO<sub>2</sub> will be prepared for comparison.

### **WP3: Catalysts characterization**

**Task 3.1 (UFU):** The catalysts prepared will be characterized by using different techniques: X-Rays Fluorescence (XRF) and Diffraction (XRD); Temperature Programmed Reduction (TPR), Oxidation (TPO), CO-, H<sub>2</sub>-, NH<sub>3</sub>-, Isopropylamine- Desorption (X-TPD); DRS UV-Vis, FTIR, and others.

**Task 3.2 (IKFT):** The catalysts prepared will be characterized by using different techniques: X-Rays Fluorescence (XRF) and Diffraction (XRD); Temperature Programmed Reduction (TPR), CO-, H<sub>2</sub>-, NH<sub>3</sub>-, Isopropylamine- Desorption (X-TPD); UV-Vis, FTIR, and others like ICP-OES, REM-EDS.

**WP4: Comparison of gas-phase (UFU) and liquid-phase (IKFT) catalytic hydrodeoxygenation (HDO) of pyrolysis and/or HTL-derived bio-oil or its representative molecules such as guaiacol, syringol, isoeugenol, levoglucosan, others.**

**Task 4.1 (UFU):** Gas-phase catalytic hydrodeoxygenation (HDO) of pyrolysis and/or HTL-derived bio-oil or its representative molecules such as guaiacol (syringol (2023-2024), isoeugenol, levoglucosan, others (2025-2026)).

**Task 4.2 (IKFT):** Liquid-phase catalytic hydrodeoxygenation (HDO) of pyrolysis and/or HTL-derived bio-oil or its representative molecules such as guaiacol, syringol, isoeugenol, levoglucosan under temperatures up to 400 °C and hydrogen pressure up to 80 bars. The upgrading using the synthesized catalysts will be conducted in batch or semi batch autoclaves



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

#### **Task 5: Evaluation of catalytic activity**

**Task 5.1 (UFU):** Catalytic tests were carried out in a continuous down-flow glass reactor with sintered plate at atmospheric pressure. Liquid guaiacol (Sigma Aldrich,  $\geq 99\%$ ) or Syringol solution (10 %wt. in decalin) was pumped (Shimadzu LC-20AT HPLC pump) and combined inside the reactor with a gas stream of  $H_2$  (White Martins,  $\geq 99.999\%$ ), whose flow rate was controlled by a MKS Type 247. The reaction temperature was measured by a thermocouple placed to the outside wall of the reactor, which was heated by an electrical furnace. After the reactor there was a glass condenser kept at 278 K. The liquid product stored in the gas-liquid separator was drained periodically for immediate analysis of the composition.

Before each run, all catalysts were reduced in situ from room temperature to 773 K for 10 h, then hold at 573 K during 2 h at a hydrogen flow of 30 mL/min, except the Pt or Ru/Nb<sub>2</sub>O<sub>5</sub> catalyst, which was reduced at 573 K at the same 12 h period of total activation. The influence of  $H_2$ /(Bio-oil key molecule - BKM) molar ratio, temperature, weight hourly space velocity (WHSV = g BKM/(h × g catalyst)), and pure catalytic support performance was analyzed. The data presented in this work correspond to the reaction in the stationary state, unless otherwise mentioned. The carbon balance was greater than 95%.

Internal and external mass transfer limitations were found to be negligible according to the tests carried out with the Pt/Nb<sub>2</sub>O<sub>5</sub> catalyst at 573 K. Internal mass transfer limitation was verified by using two particle sizes: 60–100 and 100–200 meshes. Guaiacol conversion and products selectivity did not change with the particle size, indicating that internal mass transfer limitation was negligible. The gas product stream was comprised by unreacted hydrogen, CO, CH<sub>4</sub>, other non-condensable molecules. The gases were analyzed on-line with a gas chromatograph (Shimadzu, GC-17A) equipped with a thermal conductivity detector (TCD) followed by a flame ionization detector (FID) and a HayeSep D 100/120 packed column (6 m × 3.2 mm). The heating program was 313 K for 5 min, 10 K/min to 543 K then hold 25 min, and a column flow rate of 20 mL/min argon. Quantification was performed by the external standard method using a base mixture of  $H_2$ , CO CH<sub>4</sub> in argon, which was diluted at an inert flow to give different compositions and hence a calibration curve.

The liquid product was initially identified off-line by gas chromatography-mass spectrometry (Shimadzu, GC-2010 MS). The condensable product was quantified off-line with a gas chromatograph (Shimadzu, GC-2010 FID) equipped with a FID detector and coupled to an auto sampler (AOC-20i).



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

The GC was equipped with a Phenomenex INFERNO (HT-5). The oven temperature regime was as follow: from 343 K to 443 K at 6 K/min, 1 K/min to 466 K, 6 K/min to 503 K then hold 15 min. The carrier gas (He) linear velocity was 12 cm/s, the split ratio 1/100, and the injection volume was 1  $\mu$ L. The external standard method was used for quantification, with ethanol as solvent to prepare the standard mixtures. Several liquid products (condensable ones) analyzed.

**Task 5.2 (IKFT):** Intermediate samples will be collected and analyzed during the reaction time. These intermediate and also final samples of upgraded bio-oil will be analyzed by gas chromatography, CHN/O elemental analysis and Nuclear Magnetic Resonance spectroscopy (NMR). The hydrogen consumption will be obtained by gas phase analysis. The selectivity, activity and catalyst deactivation will be analyzed through products characterization.

**WP6:** Activity and stability tests of the catalysts in continuous reactor (IKFT)

**Task 6.1 (IKFT):** Investigation of the potential of Nb<sub>2</sub>O<sub>5</sub> supported catalysts for HDO in terms of stability and activity in a continuous flow reactor with bio-oil model compound. The experiments will be conducted in a continuous flow set up using bio-oil model compounds. Different operating conditions such as catalyst: inert ratio, inlet of feed, temperature and pressure will be tested to select those, which lead to better conversion and appropriate selectivity. Finally, the catalyst activity behavior will be modeled using a simple kinetic model, as well as the conversions and selectivity in products.

**Task 6.2 (IKFT):** Evaluation of the best performing catalysts for the hydrotreatment of the heavy-phase of bio-oil in the continuous set-up. Activity, selectivity and stability of the catalysts will be evaluated for the upgrading of a feedstock closer to industrial applications as the heavy-phase of flash pyrolysis. The optimized operating conditions previously investigated for model compounds will be adapted and tested with the bio-oil heavy-phase. Like the previous work package, an extensive characterization of the bio-oil and upgraded samples will be performed to access the reaction pathways within the complex feedstock.



Universidade Federal de Uberlândia



Karlsruher Institut für Technologie

6. Gantt chart

	Year	2024				2025				2026			
WP1													
WP2													
WP3	T3.1												
	T3.2												
WP4	T4.1												
	T4.2												
WP5	T5.1												
	T5.2												
WP6	T6.1												
	T6.2												

7. Finances

Most of the UFU activities in the project will be funded mainly by Brazilian government agencies (CNPq, CAPES, FAPEMIG). The budget covers all activities in Brazil and the flight costs to Europe. The Brazilian PhD/DSc/Graduate students may also have 6 – 12 months of scholarship to stay in Europe (for which they must apply to). The Brazilian undergraduate students may also apply to international cooperation scholarships in specific project calls. KIT will finance its work by and within the Helmholtz Program MTET Topic 5. Guest stays of KIT in Brazil will be covered by separate travelling funds, which will be applied for.





**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

## **Project 2**

### **1. Project title:**

Drop-in fuels (jet & green diesel) production by integrating Fischer-Tropsch Synthesis and Hydroprocessing (Hidroisomerization & Hydrocracking) of key Fischer-Tropsch Synthesis product molecules.

### **2. Partners' activities:**

The project will combine the strengths of Universidade Federal de Uberlândia, in terms design, characterization and evaluation of Fischer-Tropsch Synthesis catalysts, with the strengths of the Institute of Catalysis Research and Technology (IKFT) and the Engler-Bunte-Institute (EBI) in terms of including the hydroprocessing, process simulation, and kinetics model developing of CO/CO<sub>2</sub> conversion processes, respectively.

a. Universidade Federal de Uberlândia (UFU) - Catalytic and Thermochemical Processes Research Group (GPCATT)

GPCATT/UFU will carry out the Fe, Co, Ru-based promoted or supported on Nb<sub>2</sub>O<sub>5</sub> catalysts preparation, characterization (FRX, DRX, TPR, H<sub>2</sub>-/CO-/NH<sub>3</sub>-TPD, TPO), the catalytic evaluation of the FTS (CO and/or CO<sub>2</sub> hydrogenation) and FTS followed Hydroprocessing one (downstream).

GPCATT/UFU will also investigate the best reaction condition by thermodynamics analysis.

b. Engler-Bunte-Institute (EBI)

c. Institute of Catalysis Research and Technology (IKFT)

IKFT will study the hydroprocessing catalytic system in order to integrate it with the FTS one. In other words, it aims to convert FTS products, e.g., linear paraffins,  $\alpha$ -olefins, and  $\alpha$ -alcohols into drop-in fuels such as kerosene and diesel in a downstream process. IKFT will also synthesize oxygen-containing fuels, so-called oxygenate fuels, such as oxymethylene ethers (OME). These are



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

alternative diesel fuels for a clean combustion and reduction of harmful emissions like soot and NO<sub>x</sub>. OMEs can be produced from renewables via methanol or dimethyl ether (DME) and processes with high energy efficiency and atom economy are currently developed. Another central topic is the generation of specialty fuels with well-defined composition and high purity, e.g. gasoline and biojet production from ethanol or OME as intermediate produced by CO/CO<sub>2</sub> hydrogenation. In these cases, the preferred raw materials are syngas produced by biomass residues gasification.

### **3. Goals:**

The goal of the project is to investigate and integrate CO/CO<sub>2</sub> hydrogenation with hydroprocessing catalytic processes and evaluate their kinetic models to convert CO, CO<sub>2</sub>, and/or other molecules derived from thermochemical processes into drop-in fuels and/or chemicals.

### **4. Work packages:**

**WP1:** Thermodynamics analysis (UFU, assisted by KIT partners)

Thermodynamic analysis comprising the chemical equilibrium of the gas-phase and liquid-phase. Both the equilibrium constants method and the minimization of the Gibbs free energy method will be applied.

**WP2:** Catalyst preparation – powder and maybe surface coatings (UFU and IKFT)

**Task 2.1 (UFU):** Co, Fe, and Ru-based catalysts will be prepared by using SBA-15/16, Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> as support and Mn, K, Ce, Cu, Zr, and/or Re as promoters.

**Task 2.2 (IKFT):** Conventional ZSM-12 can be prepared from a synthesis mixture using tetraethylammonium hydroxide (TEAOH, 35 wt% in water, Aldrich) as the organic MTW structure-directing agent, colloidal silica (Ludox® AS-30, 30 wt% in water, Aldrich), sodium aluminate (54 wt% Al<sub>2</sub>O<sub>3</sub>, 44 wt% Na<sub>2</sub>O and 5 wt% H<sub>2</sub>O, Riedel-Haën), distilled water and molar ratios of : SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 80; TEAOH/SiO<sub>2</sub> = 0.155; H<sub>2</sub>O/SiO<sub>2</sub> = 13; OH/SiO<sub>2</sub> = 0.155. Sodium aluminate and TEAOH are dissolved in distilled water and then added the colloidal silica. The resulting mixture (45 g) is magnetically stirred up to obtain a clear solution. Then, the synthesis mixture is transferred to a Teflon-lined stainless steel autoclave in order to crystallizing by hydrothermal treatment at 433 K during 5.5, 11 or 16.5 days under autogeneous pressure and static conditions. The obtained solids are separated by



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

filtration and then washed with distilled water, dried at 353 K and finally calcined under static air at 873 K during 7 h.

Ammonium forms of the zeolites are obtained by cation exchange with 2 N  $\text{NH}_4\text{Cl}$  solution at 90°C for 4 h. Finally, the zeolites are converted to their protonated forms by calcination in air at 500 °C for 1 h. Platinum was loaded on the protonated form of the catalysts by wet impregnation using  $\text{H}_2\text{PtCl}_6$  or  $[\text{Pt}(\text{NH}_3)_4(\text{NO}_3)]$ . A final Pt loading of 0.5 wt% is achieved. The impregnated catalysts are dried overnight in an oven at 120 °C. Reduction of the catalysts to disperse the metal is done in situ before starting the reaction, and the reduction conditions were chosen so that a relatively high dispersion of the metal is obtained.

**WP3: Catalysts characterization (UFU and IKFT)**

**Task 3.1 (UFU):** The catalysts prepared will be characterized by using different techniques: X-Rays Fluorescence (XRF) and Diffraction (XRD); Temperature Programmed Reduction (TPR), Oxidation (TPO),  $\text{CO}$ -,  $\text{H}_2$ -,  $\text{NH}_3$ -, Isopropylamine- Desorption (X-TPD); DRS UV-Vis, FTIR, and others.

**Task 3.2 (IKFT):** The catalysts prepared will be characterized by using different techniques: X-Rays Fluorescence (XRF) and Diffraction (XRD); Temperature Programmed Reduction (TPR),  $\text{CO}$ -,  $\text{H}_2$ -,  $\text{NH}_3$ -, Isopropylamine- Desorption (X-TPD); UV-Vis, FTIR, and others like ICP-OES, REM-EDS.

**WP4: Catalyst evaluation (UFU and IKFT)**

**Task 4.1 (UFU):** Catalyst evaluation under  $\text{CO}$  hydrogenation in continuously operated device at different reaction conditions (e.g. temperature, pressure, WGSV) by using fixed bed reactors. The integrated processes will be evaluated by adding the hydroprocessing catalyst downstream separated (followed) by a quartz wool from the FT one.

**Task 4.2 (IKFT):** Catalyst evaluation under dodecane and dodecene, diluted in decalin, hydroprocessing (hydroisomerization and hydrocracking) in a batch operated device at different reaction conditions (e.g. temperature, pressure, C12 and catalyst concentrations) after an experimental design. Liquid samples are collected periodically and analyzed by using a GC/MS or FID. Gas phase is collected in sample bags and injected into GC/TCD-FID

**WP5: Elaboration and evaluation of the kinetic models of the reactions which are taking place by process simulation (UFU and IKFT/EBI)**



**Universidade Federal de Uberlândia**



**Karlsruher Institut für Technologie**

**Task 5.1:** Evaluation Fischer-Tropsch and hydroprocessig kinetics models separately by using the better catalysts and then modelling the integrated process within a process simulation (IKFT, EBI).

**Task 5.2:** To be discussed later.

**6. Gantt chart**

	Year	2024				2025				2026			
WP1													
WP2	T2.1												
	T2.2												
WP3	T3.1												
	T3.2												
WP4	T4.1												
	T4.2												
WP5	T5.1												
	T5.2												

**7. Finances:**

Most of the UFU activities in the project will be funded mainly by Brazilian government agencies (CNPq, CAPES, FAPEMIG). The budget covers all activities in Brazil and the flights cost to Europe. The Brazilian PhD/DSc/Graduate students may also have 6-12 months of scholarship to stay in Europe (for which they must apply to). The Brazilian undergraduate students may also apply to international cooperation scholarships in specific project calls. KIT side will finance its work depending on the institute/group carrying out the research work, preferable within master thesis works. Guest stays of KIT staff in Brazil will be covered by separate travelling funds, which will be applied for. The exploration work in WP 2-4 will be extended beyond the first year, if additional resources can be raised.