

Enclosure 1b. Category 1 Application form – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in English on the website <https://vscentrum.be/>.

Title of the application:

[Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations](#)

Name and first name of the applicant:

[Van der Mynsbrugge Jeroen](#)

Institution:

[Ghent University](#)

Research group / department:

[Center for Molecular Modeling](#)

Title / position:

[Dr. ir. / BOF Postdoctoral Research Fellow](#)

e-mail address:

jeroen.vandermynsbrugge@ugent.be

Total computing time that is needed, in node days:

[4864](#)

Total disk storage that is applied for:

[~1 TB scratch space, ~1 TB long-term storage, \(provided by Ghent University\)](#)

1. Title of the research project (with IWETO link if available) within the framework of which computing time is applied for:

“Inzicht in de conversie van koolhydraten uit biomassa naar platformchemicaliën over Brønsted- en Lewiszure zeolieten.”
(BOF post-doc project - promotor: Prof. dr. ir. V. Van Speybroeck)

2. Short description of the research project within the framework of which computing time is applied for (max. 1 A4 in Arial 12):

Cracking of C4+ alkenes over acidic zeolites is employed in different petrochemical process to upgrade low-value product streams by increasing the yield of lighter olefins such as ethene and propene. Alkene cracking is generally accepted to occur through beta-scission of carbenium ion intermediates. In this project, we focus on the cracking of butenes on H-ZSM-5, for which recent studies have indicated that products are predominantly formed through a dimerization-cracking mechanism. According to this mechanism, C8 intermediates - butene dimers - are formed prior to the actual cracking steps. The overall product distribution is then determined by both the nature and abundance of the various C8 carbenium ions and their intrinsic beta-scission rates. However, because conformational changes and low-barrier H-shifts occur readily at typical operating temperatures (about 773K), a dynamical approach based on large-scale ab initio molecular dynamics (MD) and metadynamics (MTD) simulations is required to fully assess both aspects governing the product distribution. In this study, we will first investigate the relative abundance of different C8 carbenium ions by performing MD runs on the 16 possible skeletal isomers of a C8 chain (see Figure 1). Once the preferred position of the positive charge is determined for all carbon configurations, MTD simulations will be performed to study the actual beta-scission for all relevant C8 carbenium ion intermediates. From these MTD simulations, the free energy surface (FES) of the cracking reactions is reconstructed, and thermodynamic and kinetic data are inferred. To validate the reliability of the MTD simulations, a detailed committor analysis will be performed by generating hundreds of MD paths from the obtained FES.

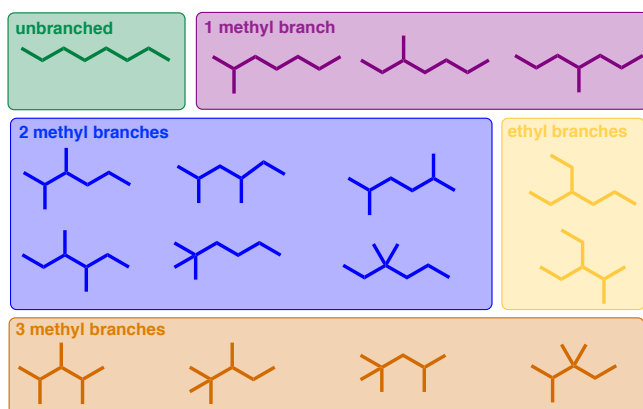


Figure 1. Schematic representation of the various possible configurations (skeletal isomers) of C8 carbenium ions.

3. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 3).

BOF post-doctoral fellowship (grant code BOF.PDO.2014.0028.01; see attachment)

4. Promoter of the research project:

Prof. dr. ir. Veronique Van Speybroeck

5. Persons mandated by the Applicant to compute on the TIER1 within the framework of the present project: Please provide for every person:
 - name and first name
 - institution
 - research group / department
 - title / position
 - experience with TIER1/TIER2 infrastructure in Belgium and abroad

Jeroen Van der Mynsbrugge

Ghent University, Center for Molecular Modeling

BOF Post-doc

5½ years of experience with TIER2 at Ghent University

1 year of experience with TIER1 at Ghent University

Pieter Cnudde

Ghent University, Center for Molecular Modeling

PhD Fellow

1 year of experience with TIER2 at Ghent University

Kristof De Wispelaere

Ghent University, Center for Molecular Modeling

FWO-PhD Fellow

1 year of experience with TIER1 at Ghent University

½ year of experience with TIER1 and TIER2 in The Netherlands

4 years of experience with TIER2 at Ghent University

Veronique Van Speybroeck

Ghent University, Center for Molecular Modeling

Full Professor

5½ years of experience with TIER2 at Ghent University

6. Description of the computing task, justification for the computing time, disk storage and memory that are applied for, and description of the software tools required (max. 3 A4 in Arial 12). Please clearly provide the following in this regard:
 - the number of nodes/cores that are applied for per computing task, with a subdivision of the computing time in sub-tasks indicating the sequence of the sub-tasks
 - whether these tasks use diversification (OpenMP, MPI, hybrid OpenMP/MPI ...)
 - the estimated memory use of a computing task (maximum 64GiB/node)

- whether a vSMP system will be used
- the requirements for disk storage (estimated volume in GiB and the total number of files), more specifically for:
 - required input files (data set, parameter files, etc.)
 - SCRATCH volume used during the performing of the computing tasks
 - result files

Large-scale ab initio molecular dynamics (AIMD) simulations will be performed with the CP2K software package, using MPI. No vSMP system will be used.

Three types of simulations will be performed, resulting in a total of over 3200 jobs. The computational requirements for this study have been carefully considered based on simulations performed on the TIER2 infrastructure at Ghent University (delcatty cluster).

Table 1 summarizes the estimated node and core days required for each simulation type:

- For the **16** different configurations (skeletal isomers) of the C8 chain, **MD simulations** in the NPT ensemble at 773 K, with an average duration of 100 ps will be performed to assess the preferential position of the positive charge and to estimate the relative abundance of the various C8+ carbenium ions. Given the size of the system under study (H-ZSM-5 unit cell + C8 guest molecule; 289+24=313 atoms), each of these simulations requires about **50 node days**.
- For all carbenium ions with a non-negligible abundance (on average 1 for each of the **16** configurations of the C8 chain), **MTD simulations of the beta-scission** reaction will be performed. Typical simulation times amount to 100 – 200 ps, depending on the height of the free energy barrier of the reaction and the number of collective variables required to consider in the simulation. Depending on the characteristics of the different reactions, each simulation will take up to **120 node days**.
- To assess the quality of the results obtained from the MTD simulations, a **committor analysis (CA)** will be performed by generating hundreds of AIMD paths starting from the trajectory of

each of the **16** MTD runs. Based on test simulations performed on delcatty, the time to generate 1 path is estimated to be about **18 node hours** for systems with unit cells as large as H-ZSM-5. To obtain sufficient sampling for statistical relevant results, it is estimated that at least **200 paths** will have to be generated for each of the MTD runs.

Table 1. Estimated core and node days required for the project.

Job type	# of simulations	Node days per simulation	Total node days	Total core days
MD	16	50	800	12800
MTD	16	120	1920	30720
CA	16	200 x 0.67	2144	34304
			4864	77824

Table 2 summarizes the requirements for scratch space and long-term storage for each simulation type. Because of the long simulation times, a complete MD or MTD trajectory cannot be obtained within the wall time limit of 72 hours, but rather requires several restarts. As a result, the scratch volume per MD or MTD simulation is relatively low.

Table 2. Estimated scratch space and long-term storage requirements for the project.

Job type	Scratch [GB/run]	Long-term storage [GB/run]	Total scratch [GB]	Total long-term storage [GB]
MD	2	10	$16 \cdot 2 = 32$	$16 \cdot 10 = 160$
MTD	1	5	$16 \cdot 2 = 32$	$16 \cdot 10 = 160$
CA	0.2	0.2	$16 \cdot 200 \cdot 0.2 = 640$	$16 \cdot 200 \cdot 0.2 = 640$
			704	960

Scaling of the CP2K software on the TIER1 has been thoroughly tested by pilot user Andy Van Yperen–De Deyne. These tests have demonstrated that excellent scaling is obtained up to 64 cores for a system of similar size (Figure 2).

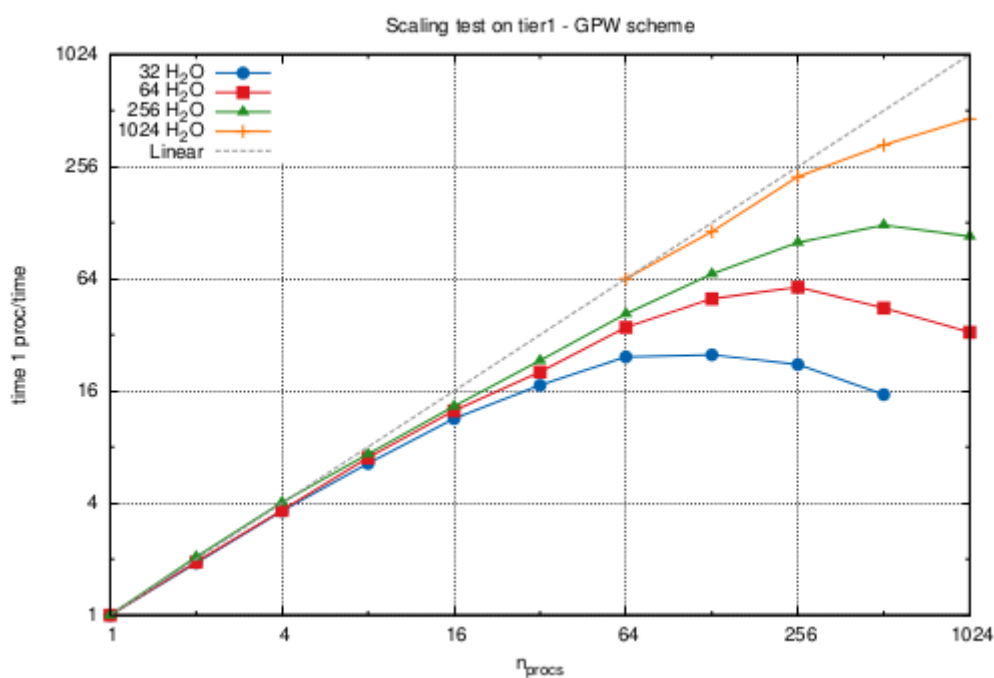


Figure 2. Efficiency vs. number of CPUs for various system sizes with the GPW code of CP2K.

7. Please indicate why the TIER1 is the appropriate machine to perform the computing task (max. 1/2 A4 in Arial 12):

Performing all simulations proposed in this project will involve the execution of over 3200 jobs, and will require more than 5000 node days in computing time. To complete this project within a reasonable timeframe, the ability to run several multi-node jobs simultaneously on the TIER1 infrastructure will be indispensable. The large number of simulations and the long simulation times required for attaining statistically relevant data has long prohibited the application of molecular dynamics methods to the study of zeolite-catalyzed reactions, but nowadays the application of advanced molecular dynamics simulations in heterogeneous catalysis research is quickly gaining momentum. The Center for Molecular Modeling was among the first research groups to successfully apply metadynamics for studying the mechanism and kinetics of zeolite-catalyzed reactions (S.L.C. Moors et al, *ACS Catal.*, 2013, 2556-2567; J. Van der Mynsbrugge, et al., *ChemCatChem*, 2014, 1906-1918). Access to the highly efficient TIER1 infrastructure with its fast nodes and inter-nodal communication will be indispensable to enable us to make further high-impact contributions to this highly competitive field.

Summary of the software required to perform the computing task, and possible installation and compilation instructions (max. 2 A4 in Arial 12). Please clearly provide the following per item in this regard:

- a reference to the software's web page
- the software licence system (open source, GPL, etc.)
- if there is no free academic use of the software, state which licence makes the installation and the use valid on the TIER1 by the Applicant (+ add a copy of the signed licence)
- if need be, which licence server will be used (name + IP address)
- whether the software is already available on the TIER1 (see <https://vscentrum.be/nl/tier1-rekenen>) and, if this is not the case, compilation and installation instructions (possibly with reference to existing TIER2 installation)

Molecular dynamics simulations will be performed using the CP2K software package (<http://www.cp2k.org/>), which is freely available under the GPL license. The required version of the programme (CP2K/20130228-ictce-4.1.13) is already available on TIER1.

8. Period during which the task is to be performed:

We estimate the proposed simulations can be completed over a time period of approximately **6 months**, preferably **starting in January 2015**.

This estimated timeframe takes into account the actual runtime of the simulations, as well as intermediate data analysis tasks and frequent job restarts.

9. Describe the results that were obtained within the framework of computing time that was attributed during the past two years on the TIER1 or on other TIER1 or TIER0 supercomputers (max. 2 A4 in Arial 12):

Over the last two years, the molecular dynamics approach suggested in this project has lead to important results that have been reported in various papers either already published or submitted for publication in high impact journals (see list below). Simulations for these projects have been performed on the TIER2 infrastructure at Ghent University, and most recently also on the TIER1. These past experiences have clearly demonstrated the added value of being able to access the TIER1 infrastructure, which has allowed us to perform more extensive studies and to obtain more accurate data in a considerably shorter timeframe.

- S. L. C. Moors, K. De Wispelaere, J. Van der Mynsbrugge, M. Waroquier, and V. Van Speybroeck, "Molecular Dynamics Kinetic Study on the Zeolite-Catalyzed Benzene Methylation in ZSM-5", *ACS Catalysis* (2013) 2556-2567.

- J. Van der Mynsbrugge, S. Moors, K. De Wispelaere, and V. Van Speybroeck, "Insight into the Formation and Reactivity of Framework-Bound Methoxide Species in H-ZSM-5 from Static and Dynamic Molecular Simulations", *ChemCatChem*, (2014) 1906-1918.
- M. Westgård Erichsen, K. De Wispelaere, K. Hemelsoet, S. L. C. Moors, T. Deconinck, M. Waroquier, S. Svelle, V. Van Speybroeck, and U. Olsbye, "How zeolitic acid strength and composition alter the reactivity of alkenes and aromatics towards methanol", *Journal of Catalysis*, submitted.

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
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