


Articles

Fossil Fuels

5573  **Numerical Predictions of Experimentally Observed Methane Hydrate Dissociation and Reformation in Sandstone**
Knut A. Birkedal,* C. Matt Freeman, George J. Moridis, and Arne Graue
dx.doi.org/10.1021/ef500255y

5587 **Characterization of Coalbed Methane Reservoirs at Multiple Length Scales: A Cross-Section from Southeastern Ordos Basin, China**
Yong Li,* Dazhen Tang, Derek Elsworth, and Hao Xu
dx.doi.org/10.1021/ef500449s

5596 **Characterization of Oxygen-Containing Species in Methanolysis Products of the Extraction Residue from Xianfeng Lignite with Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry**
Fang-Jing Liu, Xian-Yong Wei,* Rui-Lun Xie, Yu-Gao Wang, Wei-Tu Li, Zhan-Ku Li, Peng Li, and Zhi-Min Zong
dx.doi.org/10.1021/ef501414g

5606 **Optimization of a Low-Concentration *Bacillus subtilis* Strain Biosurfactant toward Microbial Enhanced Oil Recovery**
M. Souayah, Y. Al-Wahaibi,* S. Al-Bahry, A. Elshafie, A. Al-Bemani, S. Joshi, A. Al-Hashmi, and M. Al-Mandhari
dx.doi.org/10.1021/ef500954u

5612 **Low-Temperature Oxidation Characteristics of Lignite Chars from Low-Temperature Pyrolysis**
Fanrui Meng, Arash Tahmasebi, Jianglong Yu,* Huan Zhao, Yanna Han, John Lucas, and Terry Wall
dx.doi.org/10.1021/ef501004t

5623 **Preparation and Steam Gasification of Fe-Ion Exchanged Lignite Prepared with Iron Metal, Water, and Pressurized CO₂**
Hyun-Seok Kim, Shinji Kudo, Koyo Norinaga, and Jun-ichiro Hayashi*
dx.doi.org/10.1021/ef5010418

5632 **Hydrocarbon Generation Kinetics of Lacustrine Yanchang Shale in Southeast Ordos Basin, North China**
Shuangbiao Han,* Brian Horsfield, Jinchuan Zhang, Qian Chen, Nicolaj Mahstedt, Rolando di Primio, and Guolin Xiao
dx.doi.org/10.1021/ef501011b

5640	dx.doi.org/10.1021/ef501160f	Safely Burning High Alkali Coal with Kaolin Additive in a Pulverized Fuel Boiler Linlin Xu, Jie Liu, Yong Kang,* Yongqi Miao, Wei Ren, and Taotao Wang	dx.doi.org/10.1021/ef501402x	5721	Effects of Solid Residence Time and Inherent Metal Cations on the Fate of the Nitrogen in Coal during Rapid Pyrolysis Naoto Tsubouchi*
5649	dx.doi.org/10.1021/ef501230c	Influence of Different Compound Classes on the Formation of Sediments in Fossil Fuels During Aging Ruben Epping, Stefanie Kerkerling, and Jan T. Andersson*	dx.doi.org/10.1021/ef5014055	5729	Influence of Coalification on the Pore Characteristics of Middle-High Rank Coal Fei Wang, Yuanping Cheng,* Shouqing Lu, Kan Jin, and Wei Zhao
5657	dx.doi.org/10.1021/ef5012337	Determination of the Content of C_{50} Tetraacids in Petroleum Paul A. Sutton* and Steven J. Rowland	dx.doi.org/10.1021/ef5014264	5737	Heavy Oil Production by Electromagnetic Heating in Hydraulically Fractured Wells Alfred Dawletbaev, Liana Kovaleva, and Tayfun Babadagli*
5670	dx.doi.org/10.1021/ef501247h	Complete Group-Type Quantification of Petroleum Middle Distillates Based on Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GC \times GC-TOFMS) and Visual Basic Scripting Maximilian K. Jennewein,* Markus Eschner, Thomas Gröger, Thomas Wilharm, and Ralf Zimmermann	dx.doi.org/10.1021/ef501435q	5745	Dynamic Modeling of Biogas Upgrading in Hollow Fiber Membrane Contactors Yunfei Yan,* Zhen Zhang, Li Zhang, Yanrong Chen, and Qiang Tang
5682	dx.doi.org/10.1021/ef501264v	Effect of the Devolatilization Process on PM_{10} Formation during Oxy-fuel Combustion of a Typical Bituminous Coal Chang Wen, Dunxi Yu,* Jianpei Wang, Jianqun Wu, Hong Yao, and Mingzhou Xu*	dx.doi.org/10.1021/ef501656f	5756	Investigation of the Influence of the Furnace Temperature on Slagging Deposit Characteristics Using a Digital Image Technique Hao Zhou,* Bin Zhou, Letian Li, and Hailong Zhang
5690	dx.doi.org/10.1021/ef501305s	Enhancement of Gasification Reactivity of Low-Rank Coal through High-Temperature Solvent Treatment Xian Li, Ryuichi Ashida, Mitsunori Makino, Atsushi Nishida, Hong Yao, and Kouichi Miura*	dx.doi.org/10.1021/ef500570t	5766	Analysis of Syngas Quality from Portuguese Biomasses: An Experimental and Numerical Study Valter Silva, Eliseu Monteiro, Nuno Couto, Paulo Brito, and Abel Rouboa*
5696	dx.doi.org/10.1021/ef500813x	Hydrocarbon Group-Type Analysis of Petroleum-Derived and Synthetic Fuels Using Two-Dimensional Gas Chromatography Richard C. Striebig,* Linda M. Shafer, Ryan K. Adams, Zachary J. West, Matthew J. DeWitt, and Steven Zabarnick	dx.doi.org/10.1021/ef500717p	5778	Promoting Hydrolytic Hydrogenation of Cellulose to Sugar Alcohols by Mixed Ball Milling of Cellulose and Solid Acid Catalyst Yuhé Liao, Qiying Liu, Tiejun Wang, Jinxing Long, Qi Zhang, Longlong Ma,* Yong Liu, and Yuping Li
5707	dx.doi.org/10.1021/ef501362r	Method for Estimating Oil Viscosity via Dielectric Spectroscopy W. H. Hunter, Woodward,* Hagar Zohar, Robbyn Prange, Rakesh Srivastava, David Brennan, Suraj Deshmukh, and Jeff Mitchell	dx.doi.org/10.1021/ef500754d	5785	Fractionation of Bio-Oil Christian Lindfors,* Eeva Kuoppala, Anja Oasmaa, Yrjö Solantausta, and Vesa Arpiainen
5714	dx.doi.org/10.1021/ef501391g	<i>N,N</i> -Dimethylhydrazidoacrylamides. Part 1: Copolymers with <i>N</i> -Isopropylacrylamide as Novel High-Cloud-Point Kinetic Hydrate Inhibitors Mohamed F. Mady and Malcolm A. Kelland*	dx.doi.org/10.1021/ef5012808	5792	Hydrothermal Liquefaction of the Microalgae <i>Phaeodactylum tricornutum</i> : Impact of Reaction Conditions on Product and Elemental Distribution Per Sigaard Christensen, Gaël Peng, Frédéric Vogel, and Bo Brummerstedt Iversen*

- 5804 **6** Catalytic Fast Pyrolysis of Biomass Pretreated by Torrefaction with Varying Severity
Anqing Zheng, Zengli Zhao,* Zhen Huang, Kun Zhao, Guoqiang Wei, Xiaobo Wang, Fang He, and Halbin Li
dx.doi.org/10.1021/ef500892k
- 5812 CO₂ Char Gasification Rates of Sawdust, Switchgrass, and Corn Stover in a Pressurized Entrained-Flow Reactor
Aaron D. Lewis, Emmett G. Fletcher, and Thomas H. Fletcher*
dx.doi.org/10.1021/ef500903c
- 5826 HCl Emission Characteristics during the Combustion of Eucalyptus Bark
Zeqiong Xie* and Xiaoqian Ma
dx.doi.org/10.1021/ef5009242
- 5834 The Use of Acid-Activated Montmorillonite as a Solid Catalyst for the Production of Fatty Acid Methyl Esters
Leandro Zatta, Eduardo José Mendes Palva, Marcos Lúcio Corazza, Fernando Wypych, and Luiz Perreira Ramos*
dx.doi.org/10.1021/ef500935q
- 5841 Syngas as an Additional Energy Carrier in the Pulp and Paper Industry: A Mill-Wide System Analysis of a Combined Drying Concept, Utilizing On-Site Generated Gas and Steam
Christer Gustavsson,* Lars Nilsson, and Roger Renström
dx.doi.org/10.1021/ef5010144
- 5849 Quantitation of Aging Products Formed in Biodiesel during the Rancimat Accelerated Oxidation Test
Stephanie Flitsch, Philipp Marco Neu, Sigurd Schober, Norbert Kienzl, Jörg Ullmann, and Martin Mittelbach*
dx.doi.org/10.1021/ef501118r
- 5857 Effects of Torrefaction on the Pyrolysis Behavior and Bio-Oil Properties of Rice Husk by Using TG-FTIR and Py-GC/MS
Dengyu Chen,* Jianbin Zhou, and Qisheng Zhang
dx.doi.org/10.1021/ef501189p
- 5864 The Formation of Rhamnolipid-Based Water-Containing Castor Oil/Diesel Microemulsions and Their Potentiality as Green Fuels
Ren Zhu, Jie Liang,* Xing-zhong Yuan,* Le-le Wang, Li-jian Leng, Hui Li, Hua-jun Huang, Xue-Li Wang, Shan-Xing Li, and Guang-ming Zeng
dx.doi.org/10.1021/ef501307e
- 5872 Hydrodeoxygenation of Stearic Acid into Normal and Iso-Octadecane Biofuel with Zeolite Supported Palladium-Oxalate Catalyst
O. B. Ayodele,* Hazzim F. Abbas, and Wan Mohd Ashri Wan Daud*
dx.doi.org/10.1021/ef501325g

- 5882 Effects of the Torrefaction Conditions on the Fixed-Bed Pyrolysis of Norway Spruce
C. Branca, C. Di Blasi,* A. Galgano, and M. Broström
dx.doi.org/10.1021/ef501395b
- 5892 Online Measurement of Elemental Yields, Oxygen Transport, Condensable Compounds, and Heating Values in Gasification Systems
Mikael Israelsson,* Anton Larsson, and Henrik Thunman
dx.doi.org/10.1021/ef501433n
- 5902 **6** Examination of Kinetics of Non-catalytic Steam Gasification of Biomass/Lignite Chars and Its Relationship with the Variation of the Pore Structure
Shinji Kudo,* Yasuyo Hachiyama, Hyun-Seok Kim, Koyo Noninaga, and Jun-ichiro Hayashi
dx.doi.org/10.1021/ef501517n
- 5909 Hydrocarbon Liquid Production from Biomass via Hot-Vapor-Filtered Fast Pyrolysis and Catalytic Hydroprocessing of the Bio-oil
Douglas C. Elliott,* Huamin Wang, Richard French, Steve Deutch, and Kristina Iisa
dx.doi.org/10.1021/ef501536j
- 5918 **6** Maximizing the Stability of Pyrolysis Oil/Diesel Fuel Emulsions
Jonathan A. Martin, Charles A. Mullen, and Akwasi A. Boateng*
dx.doi.org/10.1021/ef5015583
- Environmental and Carbon Dioxide Issues**
- 5930 Oxidative Absorption of Hydrogen Sulfide by Iron-Containing Ionic Liquids
Jianhong Wang* and Weidong Zhang
dx.doi.org/10.1021/ef500527w
- 5936 Mg(OH)₂ for CO₂ Capture from High-Pressure, Moderate-Temperature Gas Streams
James C. Fisher II* and Ranjani V. Srinwardane
dx.doi.org/10.1021/ef500841h
- 5942 Use of Low-Volatile Solid Fuels in a 100 kW Chemical-Looping Combustor
Carl Linderholm,* Matthias Schmitz, Pavleta Knutsson, Malin Källén, and Anders Lyngfelt
dx.doi.org/10.1021/ef501067b
- 5953 Mineral Carbonation of Red Gypsum for CO₂ Sequestration
Omeid Rahmani,* Radzuan Junin, Mark Tyrer, and Rahmat Mohsin
dx.doi.org/10.1021/ef501265z

- 5959 [dx.doi.org/10.1021/ef501358j](https://doi.org/10.1021/ef501358j)
Effects of Various Factors on the Conversion Efficiency of Urea Solution in a Urea Selective Catalytic Reduction System
Kun Woo Ku, Jung Goo Hong,* Cheol Woo Park, Kyung Yul Chung, and Sang Ho Sohn
- 5968 **5** [dx.doi.org/10.1021/ef501374x](https://doi.org/10.1021/ef501374x)
Phase-Change Ionic Liquids for Postcombustion CO₂ Capture
Samuel Seo, Luke D. Simoni, Mengting Ma, M. Aruni Desilva, Yong Huang, Mark A. Stadther, and Joan F. Brennecke*
- 5978 [dx.doi.org/10.1021/ef5014677](https://doi.org/10.1021/ef5014677)
Chemical-Looping Combustion with Fuel Oil in a 10 kW Pilot Plant
Patrick Moldenhauer,* Magnus Rydén, Tobias Mattsson, Ali Hoteit, Aqil Jamal, and Anders Lyngfelt
- Efficiency and Sustainability**
- 5988 **5** [dx.doi.org/10.1021/ef5009874](https://doi.org/10.1021/ef5009874)
Life Cycle Assessment of Natural Gas-Powered Personal Mobility Options
Qiang Dai and Christian M. Lastoskie*
- 5998 [dx.doi.org/10.1021/ef501568b](https://doi.org/10.1021/ef501568b)
Synthesis of a Novel Dendrimer-Based Demulsifier and Its Application in the Treatment of Typical Diesel-in-Water Emulsions with Ultrafine Oil Droplets
Xing Yao, Bin Jiang, Luhong Zhang,* Yongli Sun, Xiaoming Xiao, Zhiheng Zhang, and Zongxian Zhao
- Catalysis and Kinetics**
- 6006 [dx.doi.org/10.1021/ef5006786](https://doi.org/10.1021/ef5006786)
Vegetable Oil Transesterification in Supercritical Conditions Using Co-solvent Carbon Dioxide over Solid Catalysts: A Screening Study
B. Saez, A. Santana, E. Ramirez, J. Maçaira, C. Ledesma, J. Llorca, and M. A. Larrayoz*
- 6012 [dx.doi.org/10.1021/ef5008825](https://doi.org/10.1021/ef5008825)
Deactivation Kinetics Model of H₂S Removal over Mesoporous LaFeO₃/MCM-41 Sorbent during Hot Coal Gas Desulfurization
Yong Son Hong, Z. F. Zhang, Z. P. Cai, X. H. Zhao, and B. S. Liu*
- 6019 **5** [dx.doi.org/10.1021/ef5009314](https://doi.org/10.1021/ef5009314)
Experimental and Modeling Investigation of *n*-Decane Pyrolysis at Supercritical Pressures
Zhenjian Jia, Hongyan Huang, Weixing Zhou,* Fei Qi, and Meirong Zeng
- 6029 **5** [dx.doi.org/10.1021/ef501263m](https://doi.org/10.1021/ef501263m)
Modeling and Simulation of Oil Sludge Pyrolysis in a Rotary Klin with a Solid Heat Carrier: Considering the Particle Motion and Reaction Kinetics
Zhengzhao Ma, Ningbo Gao, Lei Zhang, and Alimin Li*

- 6038 [dx.doi.org/10.1021/ef501326k](https://doi.org/10.1021/ef501326k)
Catalytic Degradation of High-Density Polyethylene over a Clay Catalyst Compared with Other Catalysts
Mi Liu, Jian K. Zhuo,* Si J. Xiong, and Qiang Yao
- Combustion**
- 6046 [dx.doi.org/10.1021/ef5006836](https://doi.org/10.1021/ef5006836)
Moderate or Intense Low Oxygen Dilution (MILD) Combustion Characteristics of Pulverized Coal in a Self-Regenerative Furnace
Manabendra Saha,* Bassam B. Dally, Paul R. Medwell, and Emmet M. Cleary
- 6058 [dx.doi.org/10.1021/ef500958x](https://doi.org/10.1021/ef500958x)
Evaluation of a Heat Exchanger Designed for Efficient Fine Particle Precipitation in Small-Scale Wood Combustion
J. Grigonyte,* I. Nuutinen, T. Kojonen, H. Lamberg, J. Tissari, J. Jokiniemi, and O. Sippula
- 6066 [dx.doi.org/10.1021/ef5009677](https://doi.org/10.1021/ef5009677)
Reaction Characteristics of CO and Sintering Ore Used as an Oxygen Carrier in Chemical Looping Combustion
Xun-Liang Liu,* Xiao-Jun Yin, and Hao Zhang
- 6077 [dx.doi.org/10.1021/ef501171n](https://doi.org/10.1021/ef501171n)
Effects of Equivalence Ratio and Turbulent Velocity Fluctuation on Early Stages of Pulverized Coal Combustion Following Localized Ignition: A Direct Numerical Simulation Analysis
Tamir Brosh* and Nilanjan Chakraborty
- 6089 [dx.doi.org/10.1021/ef501175v](https://doi.org/10.1021/ef501175v)
Experimental Investigation on NO_x Reduction Potential of Gas-Fired Coal Preheating Technology
Changchun Liu, Shien Hui,* Su Pan, Hao Zou, Geng Zhang, and Denghui Wang
- 6098 [dx.doi.org/10.1021/ef5011868](https://doi.org/10.1021/ef5011868)
Experimental Study on Influences of Physical Factors to Supercritical RP-3 Surface and Liquid-Space Thermal Oxidation Coking
Zhi Tao, Yanchen Fu,* Guoqiang Xu, Hongwu Deng, and Zhouxia Jia
- 6107 **5** [dx.doi.org/10.1021/ef501313x](https://doi.org/10.1021/ef501313x)
High-Pressure Study of Methyl Formate Oxidation and Its Interaction with NO
Lorena Marrodán, Ángela Millera, Rafael Bilbao, and María U. Alzueta*
- 6116 **5** [dx.doi.org/10.1021/ef501269j](https://doi.org/10.1021/ef501269j)
Mitigation of Fireside Corrosion in Power Plants: The Combined Effect of Sulfur Dioxide and Potassium Chloride on the Corrosion of a FeCrAl Alloy
K. Hellström,* J. Hall, P. Malmberg, Y. Cao, M. Norell, and J.-E. Svensson

6130 **6** dx.doi.org/10.1021/ef501380cPyrolysis of Medium-Density Fiberboard: Optimized Search for Kinetics Scheme and Parameters via a Genetic Algorithm Driven by Kissinger's Method
Kai-Yuan Li, Xinyan Huang, Charles Fleischmann, Guillermo Rein, and Jie Ji*

6140 dx.doi.org/10.1021/ef501386g

Utilization of Sewage-Sludge-Derived Hydrochars toward Efficient Cocombustion with Different-Rank Coals: Effects of Subcritical Water Conversion and Blending Scenarios
Chao He,* Ke Wang, Yanhui Yang, and Jing-Yuan Wang***Process Engineering**6151 **6** dx.doi.org/10.1021/ef501086vExperimental Investigation on the Effect of Aliphatic Ionic Liquids on the Solubility of Heavy Crude Oil Using UV-Visible, Fourier Transform-Infrared, and ¹³C NMR Spectroscopy
Sivabalan Sakthivel, Sugirtha Velusamy, Ramesh L. Gardas, and Jitendra S. Sangwai*6163 **6** dx.doi.org/10.1021/ef5011385Structures and Wettability Alterations of a Series of Bispyridinium Dibromides Exchanged with Reduced-Charge Montmorillonites
Zhongxin Luo, Manglai Gao,* Zheng Gu, and Yage Ye6172 **6** dx.doi.org/10.1021/ef501169mDemulsification of Oleic-Acid-Coated Magnetite Nanoparticles for Cyclohexane-in-Water Nanoemulsions
Jiling Liang, Haiping Li, Jingen Yan, and Wanguo Hou***Numerical Predictions of Experimentally Observed Methane Hydrate Dissociation and Reformation in Sandstone**Knut A. Birkedal,^{#,||,L,F} C. Matt Freeman,^{L,F} George J. Moridis,^{L,H,S} and Arne Graue^{L,F}[†]Department of Physics and Technology, University of Bergen, 5200 Bergen, Norway[‡]Hilcorp Energy Company, Houston, Texas 77002, United States[§]Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States**Supporting Information**

ABSTRACT: Numerical tools are essential for the prediction and evaluation of conventional hydrocarbon reservoir performance. Gas hydrates represent a vast natural resource with a significant energy potential. The numerical codes/tools describing processes involved during the dissociation (induced by several methods) for gas production from hydrates are powerful, but they need validation by comparison to empirical data to instill confidence in their predictions. In this study, we successfully reproduce experimental data of hydrate dissociation using the TOUGH+HYDRATE (T+H) code. Methane (CH₄) hydrate growth and dissociation in partially water- and gas-saturated Bentheim sandstone were spatially resolved using Magnetic Resonance Imaging (MRI), which allows the in situ monitoring of saturation and phase transitions. All the CH₄ that had been initially converted to gas hydrate was recovered during depressurization. The physical system was reproduced numerically, using both a simplified 2D model and a 3D grid involving complex Voronoi elements. We modeled dissociation using both the equilibrium and the kinetic reaction options in T+H, and we used a range of kinetic parameters for sensitivity analysis and curve fitting. We successfully reproduced the experimental results, which confirmed the empirical data that demonstrated that heat transport was the limiting factor during dissociation. Dissociation was more sensitive to kinetic parameters than anticipated, which indicates that kinetic limitations may be important in short-term core studies and a necessity in such simulations. This is the first time T+H has been used to predict empirical nonmonotonic dissociation behavior, where hydrate dissociation and reformation occurred as parallel events.

INTRODUCTION

Gas hydrate is a solid state of special gases (capable of forming hydrates) and water, in which hydrogen bonding and van der Waals interaction forces provide stability to the crystal structure. Of the various hydrate-forming gases in natural hydrates, methane (CH₄) is overwhelmingly the most common. The CH₄-hydrate stability is governed by pressure and temperature, and its hydration reaction is commonly described by



where the hydration number N_1 is estimated to be 5.99 ± 0.07 .¹

Vast resources are associated with gas hydrates,² and depressurization is often considered one of the more promising approaches for hydrate dissociation.³ Dissociation requires less energy relative to thermal methods but is limited by the endothermic reaction and therefore relies on heat transfer from the surroundings.

Numerical modeling is a valuable tool for conventional oil and gas production. Space and time are discretized into a finite number of subdivisions, where coupled equations describe the physical and chemical conditions of each subdomain. A range of simulation tools are available for hydrate simulation.⁴ Several case studies have been performed due to limited field data,^{5–10} while others use field specific parameters for evaluation.^{11–19} Code verification has been performed through comparison with available production data and open-hole pressure-response

tests.^{20,11,21,22} A series of studies have also aimed at code-validation through comparison with experimental data.^{23–31} This study compares experimental dissociation data with numerical data in order to determine the robustness and advantages of numerical modeling.

T+H³² is a multicomponent, multiphase fluid and heat flow simulator that describes hydrate formation and dissociation through coupled equations of mass and heat balance. These processes are predicted by an equilibrium and kinetic model. Phase transitions in the equilibrium model are governed by temperature and pressure, where the different phase combinations are described in Figure 1.⁷ The kinetic model is described by an Arrhenius-type equation, where kinetic parameters are considered in addition to temperature and pressure. In a study involving several gas hydrate configurations and long-term production, the equilibrium and the kinetic models exhibited a similar dissociation response.³³ In short-term processes (such as laboratory studies of dissociation in core samples that lasted a few hours), the kinetic and the equilibrium models exhibited significantly different behavior, which converged as time advanced. Thus, Kowalsky and Moridis (2007)³³ recommended the use of the kinetic model in short-term processes.

The kinetic model is based on the work of Bishnoi and co-workers^{34,35} but was modified to account for geometry

Received: January 21, 2014

Revised: August 20, 2014

Published: August 25, 2014

5573

© 2014 American Chemical Society

ACS Publications

Energy & Fuels, Volume 28, Issue 9

12A

6 Supporting Information available via online article

dx.doi.org/10.1021/ef501086v | Energy Fuels 2014, 28, 5573–5586