# THERMAL AND THERMO-CATALYTIC PROCESSES FOR HEAVY OIL CONVERSION

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Авторите биха искали да благодарят на „ЛУКОЙЛ Нефтохим Бургас“ АД за техническата база и подкрепата, без които издаването на тази монография би било невъзможно. Целта на книгата, която се явява оригинален принос в химията и технологията на тежките нефтени фракции, е да разпространява натрупания опит в тази област от човешкото познание. Тя е предназначена за студенти, аспиранти и инженери, работещи в областта на химията и технологията на тежките нефтени остатъци.

The authors would like to thank “LUKOIL Neftohim Burgas” AD for the technical base, and the support without which the publication of this monograph would have been impossible. The aim of the book, that is an original contribution to the chemistry and technology of heavy oils, is to disseminate the accumulated experience in this field of human knowledge. It is designed for undergraduate students, PhD students, and chemical engineers working in the field of chemistry and technology of the heavy oils.

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# Contents

# Foreword

Oil refining is an industrial chemistry branch that delivers the human society with fuels which are still the main choice for driving our vehicles: automobiles, trucks, airplanes, ships, and trains. The by-products of petroleum refining provide the petrochemical building blocks materials: plastics, synthetic fibers, and synthetic elastomers. Petroleum refining business has faced many challenges lately. They concern low and volatile margins, strict environmental legislation, and tough product specifications. As a result some refineries could not survive at these conditions and the number of refineries worldwide has dropped from 750 down to 643 for the period between 2001 and 2013. At the same time the global refining capacity has been increased from 83.5 up to 92.0 million barrels per day. The refineries which did not survive were small in size and they did not have heavy oil conversion units in their processing schemes. In these difficult for refining industry times featuring with worsen quality of supplied crude oil and of oil reserves and high differential between prices of transportation fuels and heavy fuel oil the significance of bottom of the barrel upgrading processes becomes very high. The trend of decreased demand of heavy oil products additionally supports the leading role of the bottom of the barrel (BOB) upgrading technologies in the refining business. The application of BOB technologies in the petroleum refining has become a bail for surviving in this industrial chemistry branch. The proper utilization of capabilities of BOB refinery units is vital for competitiveness of any refinery. The single variable that has the biggest impact on refinery BOB conversion unit performance is the feed quality. A per cent increase of heavy oil conversion is equivalent to several million US $ per year. To select the right feed for a BOB process one needs to know more about the relationship between residual feed properties and conversion and product yields. Characterization of the residual oils plays a very important role in determination of their behavior in the refinery BOB conversion units. This book summarizes the results of the investigations on the characterization of heavy oils performed in the Research laboratory of LUKOIL Neftohim Burgas, and in the Prof. Dr. Assen Zlatarov University – Burgas for the period 2011-2016. It also deals with the results obtained in the laboratory and commercial studies of the heavy oil upgrading processes fluid catalytic cracking, visbreaking and ebullated bed hydrocra-

cking carried out in the Prof. Dr. Assen Zlatarov University – Burgas and at the commercial units in LUKOIL Neftohim Burgas refinery for the same space of time. The book is intended to shed more light on heavy oil characterization by the use of easy accessible methods, which can be available in refinery, and to relate this information to the heavy oil upgrading process performance. The book is also devoted to discussing the performance of the processes fluid catalytic cracking, thermal cracking (visbreaking), and ebullated bed residue hydrocracking in laboratory and commercial conditions.

We would like to acknowledge the valuable work of the PhD students Radoslava Nikolova, and Anife Veli during the preparation of this book. We are also indebted to our colleagues for all the support they provided.

# Preface

The economic development driven by the dramatic population, urbanization, and industrial growth recorded in recent years, has increased the demand of world oil supply. Most of this supply is met in the form of light crude oil. Therefore, the world's supply of light crude oil is depleting constantly and consequently, the demand of transportation fuels such as gasoline has increased [1]. The stock of heavy oil and petroleum residual fractions have gained significant attention in recent years to bridge the ever increasing fuel demand-supply gap for petrochemical feeds and transportation fuels [2]. Moreover, the rapidly rise in transportation fuel prices and increasingly stringent environmental regulations have diverted attention towards heavy oil upgrading in order to find cost-effective ways to ensure a constant future fuel supply. Currently, more than half of the world's oil reserves (53.3%) are in the form of restorable oils such as heavy oil, extra heavy oil, oil sand, tar sands, oil shale, and bitumen [3]. The change in crude oil quality around the world has impacted the petroleum refining industry in such a way that current and new refineries are being re-configured and designed respectively to process heavier feedstocks. These feedstocks are characterized by high amounts of impurities (sulfur, nitrogen, metals, asphaltenes) and low distillate yields, which make them more difficult to process compared with light crude oils. Contrarily, the demand of light distillates for producing of so-called clean fuels (e.g. near zero sulfur gasoline and diesel) is increasing throughout the world. These circumstances situate not only refineries but also research centers, catalyst manufacturers, and process developers in a great dilemma which need to adapt, and design future technologies for proper conversion and upgrading of heavy oils. There are various commercially available technologies to upgrade heavy oils, which are typically classified in carbon rejection and hydrogen addition processes [4]. They can be also classified as thermal and thermo-catalytic conversion processes, because all heavy oil conversion processes take place at elevated temperatures, with or without the presence of catalyst, and with or without the presence of hydrogen at higher pressure [5-8]. Despite the progress achieved in the heavy oil conversion technologies and their commercial application, there are still gaps in the knowledge about heavy oil characterization and the

effect of heavy oil properties on the thermal and thermo-catalytic processes performance, both in laboratory and commercial scale. The aim of this monograph is to shed some more light about the heavy oil characterization, performed with the available in the refinery conventional methods and the effect of heavy oil feedstock quality on yield distribution and product quality in laboratory and commercial units for thermal and thermo-catalytic processes.

358. **Petersen, J. C.** Asphalt oxidation-An overview including a new model for oxidation proposing that physicochemical factors dominate the oxidation kinetics. *Fuel Sci. Technol. Int.*, 11 (1993) 57-87.

359. **Herrington, P. R.** Oxidation of bitumen in the presence of a constant concentration of oxygen, *Petrol. Sci. Technol.*, 16 (1998) 1061-1084.

360. **Laux, H., I. Rahimian, H.-J. Neumann.** Particle distribution, colloid stability and rheological behavior of crude oil residues and bitumen. *Erdől Erdgas Kohle*, 109 (1993) 368-372.

361. **Sunyaev, Z. I.** Physicochemical technology of oil refining. *Chem. Technol. Fuels Oils*, 8 (1986) 5-7.

362. **Hashmi, S. M., A. Firoozabadi.** Effect of dispersant on asphaltene suspension dynamics: aggregation and sedimentation. *J. Phys. Chem. B*, 114 (2010) 15780-15788.

363. **Garcıa, M., L. Carbognani.** Asphaltene-paraffin structural interactions. Effect on crude oil stability. *Energy & Fuels*, 15 (2001) 1021-1027.

364. IP 375/11 Petroleum products – Total sediments in petroleum residual fuel oils.

365. **Darouich, T. A., F. Behar, C. Largeau.** Thermal cracking of the light aromatic fraction of Safaniya crude oil – experimental study and compositional modelling of molecular classes. *Org. Geochem.*, 37 (2006) 1130-1154.

366. **Voge, H. H., G. M. Good.** Thermal cracking of higher paraffins. *J. Am. Chem. Soc.*, 71 (1949) 593-597.

367. **Camp, C. V., P. V. Damme, G. Froment.** Thermal cracking of kerosene. *Ind. Eng. Chem. Process. Des. Dev.*, 23 (1984) 155-162.

368. **Watanabe, M., T. Adschiri, K. Arai.** Carbon number correlation of overall rate constant of pyrolysis of n-alkanes. (https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/45_3_WASHINGTON%20DC_08-00_0607.pdf).

369. **Watanabe, M., T. Adschiri, K. Arai.** Overall rate constant of pyrolysis of n-alkanes at a low conversion level. *Ind. Eng. Chem. Res.*, 40 (2001) 2027-2036.

370. **Morawski, I., J. M. Mosiewski.** Effects of parameters in Ni-Mo catalyzed hydrocracking of vacuum residue on composition and quality of obtained products. *Fuel Process. Technol.*, 87 (2006) 659-669.

371. **Sanchez, S., M. A. Rodriguez, J. Ancheyta.** Kinetic model for moderate hydrocracking of heavy oils. *Ind. Eng. Chem. Res.*, 44 (2005) 9409–9413.

372. **Li, S., C. Liu, G. Que, W. Liang.** Colloidal structures of vacuum residua and their thermal stability in terms of saturate, aromatic, resin and asphaltene composition. *J. Pet. Sci. Eng.*, 22 (1999) 37-45.

373. **Carillo, J. A., F. Pantoja, G. Garzón, H. Barrios, J. Fernández, E. Carmona, J. Saavedra.** Control of Severity in Visbreaking. (https://web.anl.

gov/PCS/acsfuel/preprint%20archive/Files/45_3_WASHINGTON%20DC_08-00_0617.pdf) (accessed on 16.06.2016).

374. **Rahimi, P., T. Gentzis, K. Chung, V. Nowlan, A. DelBianco.** Correlation of chemical composition of extra heavy oils with incipient coke formation using hot-stage microscopy. (https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/42_1_SAN%20FRANCISCO_04-97_0146.pdf (accessed on 16.06.2016).
375. **Zerlia, T., G. Pinelli.** Stability-related tests on visbreaking residues obtained at increasing severity. *Fuel*, 72 (1993) 1109-1114.
376. **Rogel, E.** Theoretical approach to the stability of visbroken residues. *Energy Fuels*, 12 (1998) 875-880.
377. **Higuerey, I., E. Rogel, P. Pereira.** Residue stability study in a thermal catalytic steam cracking process through theoretical estimation of the solubility parameter. *Pet. Sci. Technol.*, 19 (2001) 387-401.
378. **Bartholdy, J., S. Andersen.** Changes in asphaltene stability during hydrotreating. *Energy Fuels*, 14 (2000) 52-55.
379. **Shimizu, K., J. Uehara, T. Hayashi.** Current dtudies on dtability and combustibility of marine fuel oil. *Bulletin of the M.E.S.J.*, 28 (2000) 22-29.
380. **Stratiev, D., R. Dinkov, I. Shishkova, I. Sharafutdinov, N. Ivanova, M. Mitkova, D. Yordanov, N. Rudnev, K. Stanulov.** What is behind the high values of hot filtration test of the ebullated bed residue H-Oil hydrocracker residual oils. *Energy & Fuels*, 2016, (DOI: 10.1021/acs.energyfuels.6b01241).
381. *IP 390-11 Petroleum products – Total sediments in petroleum residual fuel oils. Part 2 Determination using standard procedures for aging*.
382. **Redelius, P. G.** Solubility parameters and bitumen. *Fuel*, 79 (2000) 27-35.
383. **Faina, R., M. Ingrassia, A. Zanotti.** A method for determining an instantaneous reference parameter of tar stability in a thermal conversion oil plant. EP 0529397 B1, 1995.
384. ASTM D-7061–06 - Standard test method for measuring n-heptane induced phase separation of asphaltene-containing heavy fuel oils as separability number by an optical scanning device.
385. **Yamchi, H. S.** *Effect of refining on asphaltene property distributions*. [Master of Science Thesis]. University of Calgary, 2014, (http://theses.ucalgary.ca/jspui/handle/11023/1619).
386. **Evdokimov, I. N.** The importance of asphaltene content in petroleum III—New criteria for prediction of incompatibility in crude oil blends. *Pet. Sci. Technol.*, 28 (2010) 1351-1357.
387. **Watkinson, P.** Deposition from Crude Oils in Heat Exchangers. *Heat Tran. Eng.*, 28 (2007) 177-184.

388. **Dickenson, R.** The move to higher value transportation fuels from residual fuel oil. *Proc. of IRPC 2014*, Verona 24.06-26.06.2014.

389. **Al-Rashidi, B.** Reshaping of refining landscape in Europe. *Proc. of IRPC 2014*, Verona 24.06-26.06.2014.

390. **Castaneda, L. C., J. A. D. Munoz, J. Ancheyta.** Current situation of emerging technologies for upgrading of heavy oils. *Catal. Today*, 220-222 (2014) 248-273.

391. **Ancheyta, J., M. Rana.** *Future technology in heavy oil processing*. (http://www.eolss.net/sample-chapters/c08/e6-185-22.pdf).

392. **Kim, J. W., D. C. Longstaff, F. V. Hanson.** Catalytic and thermal effects during hydrotreating of bitumen-derived heavy oils. *Fuel*, 77 (1998) 1815-1823.

393. **Yang, C., H. Zheng, F. Du, C. Xu.** *Reaction characteristics and mechanism of residium hydrocracking*. (Last accessed on 20.07.2016) (http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/43_3_BOSTON_08-98_0668.pdf).

394. **Li, C., T. Yang, W. Deng, H. Zhang, M. Cui.** The effects of iron (III) dodecylbenzene sulfonate on the slurry-phase hydrocracking of Venezuala fuel oil with oil soluble Mo catalyst. *Energy Fuels*, 30 (2016) 4710-4716.

395. **Zhou, X.-L., S.-Z. Chen, C.-L. Li.** A predictive kinetic model for delayed coking. *Pet. Sci. Technol.*, 25 (2007) 1539-1548.

396. **Zhou, S. L., Z. S. Zhou, M. B. Wen, C. L. Lieh, C. KeQia.** Research study on dynamic model of complex reaction of vacuum residual oil. *ACTA Petrolei Sinica (Petroleum Processing Section)*, 15 (1999) 73-78.

397. **Fukuyama, H., S. Terai.** Kinetic study on the hydrocracking reaction of vacuum residue using a lumping model. *Pet. Sci. Technol.*, 25 (2007) 277-287.

398. **Smith, G. C.** *Catalytic cracking of n- alkanes and n-alkyl benzenes over H-ZSM-5 zeolite*. [PhD Thesis]. Massachusetts Technology Institute of Technology, 1993.

399. **Wojciechowski, B. W.** The reaction mechanism of catalytic cracking: quantifying activity, selectivity, and catalyst decay. *Cat. Rev. Sci. Eng.*, 40 (1998) 209-328.

400. **Cumming, K. A., B. W. Wojciechowski.** Hydrogen transfer, coke formation, and catalyst decay and their role in the chain mechanism of catalytic cracking. *Cat. Rev. Sci. Eng.*, 38 (1996) 101-157.

401. **Kissin, Y. V.** Chemical mechanisms of catalytic cracking over solid acidic catalysts: alkanes and alkenes. *Cat. Rev. Sci. Eng.*, 43 (2001) 85-146.

402. **Bollas, G. M., I. A. Vasalos, A. A. Lappas, D. K. Iatridis, G. K. Tsioni.** Bulk molecular characterization approach for the simulation of FCC feedstocks. *Ind. Eng. Chem. Res.*, 43 (2004) 3270-3281.

403. **Raseev, S.** *Thermal and catalytic processes in petroleum refining*. Marcel Dekker, Inc. 270 Madison Avenue, New York, NY 10016, 2003.

404. **Fahim, M. A., T. A. Alsahhaf, A. Elkilani.** *Fundamentals of petroleum refining*. First ed. Elsevier, Amsterdam, The Netherlands, 2010.

405. **Pujro, R., M. Falco, U. Sedran.** Catalytic cracking of heavy aromatics and polycyclic aromatic hydrocarbons over fluidized catalytic cracking catalysts. *Energy Fuels*, 29 (2015) 1543-1549.

406. **Moldoveanu, S. C.** Pyrolysis of Hydrocarbons. In: S. C. Moldoveanu (Ed.), *Techniques and instrumentation in analytical chemistry*, Elsevier, Amsterdam, The Netherlands, 2010; 131-229.

407. **Liguras, D. K., D. T. Allen.** Structural models for catalytic cracking. 1. Model compound reactions. *Ind. Eng. Chem. Res.*, 28 (1989) 665-673.

408. **Williams, B. A., W. Ji, J. T. Miller, R. Q. Snurr, H. H. Kung.** Evidence of different reaction mechanisms during the cracking of n-hexane on H-USY zeolite. *Appl. Catal. A: Gen.*, 203 (2000) 179-190.

409. **Jolly, S., J. Saussey, M.M. Bettahar, J.C. Lavalley, E. Benazzi.** Reaction mechanisms and kinetics in the n-hexane cracking over zeolites. *Appl. Catal. A: Gen.*, 156 (1997) 71-96.

410. **Babitz, S. M., B. A. Williams, J. T. Miller, R. Q. Snurr, W. O. Haag, H. H. Kung.** Monomolecular cracking of n-hexane on Y, MOR, and ZSM-5 zeolites. *Appl. Catal. A: Gen.*, 179 (1999) 71-86.

411. **Malherbe, R. R., F. D. Castro.** Calculation of the energy of adsorption of n-paraffins in nanoporous crystalline and ordered acid catalysts, and its relationship with the activation energy of the monomolecular catalytic cracking reaction. *J. Mol. Catal. A: Chem.*, 280 (2008) 194-202.

412. **Wender, A., A. Barreau, C. Lefebvre, A. Di Lella, A. Boutin, P. Ungerer, A.H. Fuchs.** Adsorption of n-alkanes in faujasite zeolites: molecular simulation study and experimental measurements. *Adsorpt.*, 13 (2007) 439-451.

413. **Gray, M. R., W. C. McCaffrey.** Role of chain reactions and olefin formation in cracking, hydroconversion, and coking of petroleum and bitumen fractions. *Energy Fuels*, 16 (2002) 756-766.

414. **Corma, A., A. V. Orchille's.** Current views on the mechanism of catalytic cracking. *Micropor. Mesopor. Mater.*, 21 (2000) 35-36.

415. **Jentoft, F. C., B. C. Gates.** Solid-acid-catalyzed alkane cracking mechanisms: evidence from reactions of small probe molecules. *Top. Catal.*, 4 (1997) 1-13.

416. **Vafi, K.** *High Temperature Thermal Cracking of Heavy Oils*. [PhD Thesis]. University of Alberta, 2012.

417. **Konno, H. R. Ohnaka, J. Nishimura, T. Tago, Y. Nakasaka, T. Masuda.** Kinetics of the catalytic cracking of naphtha over ZSM-5 zeolite: effect of reduced crystal size on the reaction of naphthenes. *Catal. Sci. Technol.*, 4 (2014) 4265-4273.

418. **Behar, F., M. Vandenbroucke.** Experimental determination of rate constants of the n-C25 thermal cracking at 120, 140, and 800 bar: implication for high-pressure/high-temperature prospects. *Energy Fuels*, 10 (1996) 932-940.

419. **Alabi, W., L. Atanda, R. Jermy, S. Al-Khattaf.** Kinetics of toluene alkylation with methanol catalyzed by pure and hybridized HZSM-5 catalysts. *Chem. Eng. J.*, 195-196 (2012) 276-288.

420. **Al-Shammari, A. A., S. A. Ali, N. Al-Yassir, A. M. Aitani, K. E. Ogunronbi, K. A. Al-Majnouni, S. S. Al-Khattaf.** Catalytic cracking of heavy naphtha-range hydrocarbons over different zeolites structures. *Fuel Process. Technol.*, 122 (2014) 12-22.

421. **Domke, S. B., R. F. Pogue, F. J. R. Van Neer, C. M. Smith, B. W. Wojciechowski.** Investigation of the kinetics of ethylbenzene pyrolysis using a temperature-scanning reactor. *Eng. Chem. Res.*, 40 (2001) 5878-5884.

422. **Zhao, L., B. Shen, J. Gao, Ch. Xu.** Investigation on the mechanism of diffusion in mesopore structured ZSM-5 and improved heavy oil conversion. *J. Catal.*, 258 (2008) 228-234.

423. **Freund, H., W. N. Olmstead.** Detailed chemical kinetic modelling of butylbenzene pyrolysis. *Int. J. Chem. Kinet.*, 21 (1989) 561-574.

424. **Tukur, N. M., S. Al-Khattaf.** Catalytic cracking of n-dodecane and alkyl benzenes over FCC zeolite catalysts: Time on stream and reactant converted models. *Chem. Eng. Process.*, 44 (2005) 1257-1268.

425. **Behar, F., F. Lorant, H. Budzinski, E. Desavis.** Thermal stability of alkylaromatics in natural systems: kinetics of thermal decomposition of dodecylbenzene. *Energy Fuels*, 16 (2002) 831-841.

426. **Savage, P. E., M. T. Klein.** Asphaltene reaction pathways. 2. Pyrolysis of n-pentadecylbenzene. *Ind. Eng. Chem. Res.*, 26 (1987) 488-494.

427. **Leininger, J. P., F. Lorant, C. Minot, F. Behar.** Mechanism of 1-methylnaphthalene pyrolysis in a batch reactor and relevance with other methylated polyaromatics. *Energy Fuels*, 20 (2006) 2518-2530.

428. **Behar, F., H. Budzinski, M. Vandenbroucke, Y. Tang.** Methane generation from oil cracking: kinetics of 9-methylphenanthrenecracking and comparison with other pure compounds and oil fractions. *Energy Fuels*, 13 (1999) 471-481.

429. **Fabuss, B., R. Kafesjian, J. Smith, C. N. Satterfield.** Thermal decomposition rates of saturated cyclic hydrocarbons. *I&E. Proc. Des. Dev.*, 3 (1964) 248-254.

430. **Tone, S., H. Seko, H. Maruyama, T. Otake.** Catalytic cracking of methylcyclohexane over silica alumina catalyst in gas fluidized bed. *J. Chem. Eng. Jpn.*, 7 (1974) 44-51.

431. **Yan, B. P. Xu, X. Li, C. Y. Guo, Y. Jin, Y. Cheng.** Experimental study of liquid hydrocarbons pyrolysis to acetylene in H2/Ar plasma. *Plasma Chem. Plasma Process.*, 32 (2012) 1203-1214.

432. **Letzsch, W. S. A. G. Ashton.** The effect of feedstock on yields and product quality. In: J. S. Magee, M. M. Mitchell (Eds.), *Fluid Catalytic Cracking: Science and Technology Studies in Surface Science and Catalysis*, 76, Elsevier Science Publishers B.V., 1993, 441-498.

433. **Appleby, W. G., J. W. Gibson, G. M. Good.** Coke formation in catalytic cracking. *I&EC Process Des. Dev.*, 1 (1962) 102-110.

434. **Corma, A., P. J. Miguel, A. V. Orchilles.** The role of reaction temperature and cracking catalyst characteristics in determining the relative rates of protolytic cracking, chain propagation, and hydrogen transfer. *J. Catal.*, 145 (1994) 171-180.

435. **Stratiev, D., I. Shishkova.** Conversion of pyrolysis pitch and cycle oils in the fluid catalytic cracking. *Proc. 43rd International Petroleum Conference*, Bratislava, September 25th-26th, 2007.

436. **Yibin, L., T. Yongshan, L. Chunyi, Y. Chaohe.** Catalytic cracking and PSO-RBF neural network model of FCC cycle oil. *China Pet. Process. Pe.*, 15 (2013) 63-69.

437. **Yasar, M., F. E. Cerci, H. Gulensoy.** Effect of asphaltenes on pyrolysis kinetics of saturates. *J. Anal. Appl. Pyrolysis*, 56 (2000) 219-228.

438. **Karacan, O., M. VersanKok.** Pyrolysis analysis of crude oils and their fractions. *Energy Fuels*, 11 (1997) 385-391.

439. **Jacob, S., B. Gross, S. Voltz, V. W. Weekman, Jr.** A lumping and reaction scheme for catalytic cracking. *AlChE J.*, 22 (1976) 701-713.

440. **Jackson, K. J., A. K. Burnham, R. L. Braun, K. G. Knauss.** Temperature and pressure dependence of n-hexadecane cracking. *Org. Geochem.*, 10 (1995) 941-953.

441. **Ford, T. J.** Thermal decomposition of hexadecane: reaction mechanism. *Ind. Eng. Chem. Res.*, 25 (1986) 240-243.

442. **Khorasheh, F., M. R. Gray.** High-pressure thermal cracking of n-hexadecane. *Ind. Eng. Chem. Res.*, 32 (1993) 1853-1863.

443. **Chang, J., N. Tsubaki, K. Fujimoto.** Elemental sulfur as an effective promoter for the catalytic hydrocracking of Arabian vacuum residue. *Fuel*, 80 (2001) 1639-1643.

444. **Chang, J., L. Fan, K. Fujimoto.** Enhancement effect of free radical initiator on hydro-thermal cracking of heavy oil and model compound. *Energy Fuels*, 13 (1999) 1107-1108.

445. **Shi, B., X. Men, L. Guo, Z. Guo, G. Que.** Effect of free radical initiators on the hydrocracking of heavy oils. *J. Fuel Chem. Technol.*, 38 (2010) 422-427.

446. **Shi, B., X. Men, L. Guo, D. Yu, G. Que.** Effect of free radical initiators addition on the visbreaking of vacuum residues. *J. Fuel Chem. Technol.*, 38 (2010) 696-700.

447. **Chang, J., Y. Fu, Y. Shibata, M. Yoshimoto, K. Fujimoto, N. Tsubaki.** Promotional effect of oxidation pretreatment on hydro-thermal cracking of Canadian oil sand bitumen. *Fuel*, 84 (2005) 1661-1663.

448. **Chang, J., K. Fujimoto, N. Tsubaki.** Effect of initiative additives on hydro-thermal cracking of heavy oils and model compound. *Energy Fuels*, 17 (2003) 457-461.

449. **Gilbert, W., C. Baptista, M. A. Teixeira.** Calculating atmospheric residue FCC product slate. *PTQ Q1* (2001) 49-53.

450. **Ferrer, C.-A.B.** Prediction of physicochemical properties of FCC feedstock by chemometric analysis of their ultraviolet spectrum, C.T.F. *Cienc. Tecnol. Futuro*, 3 (2008) 143-146.

451. **Li, Z., J. Gao, G. Wang, Q. Shi, Ch. Xu.** Influence of nonbasic nitrogen compounds and condensed aromatics on coker gas oil catalytic cracking and their characterization. *Ind. Eng. Chem. Res.*, 50 (2011) 9415-9424.

452. **Voltz, S. E., D. M. Nace, V. W. Weekman Jr.** Application of a kinetic model for catalytic cracking. Some correlations of rate constants. *Ind. Eng. Chem. Process Des. Dev.*, 10 (1971) 538-541.

453. **Juárez, J. A., F. L. Isunza, E. A. Rodriguez.** Correlations for predicting the effect of feedstock properties on catalytic cracking kinetic parameters. *Ind. Eng. Chem. Res.*, 37 (1998) 4637-4640.

454. **Lappas, A. A., D. K. Iatridis, M. C. Papapetrou, E. P. Kopalidou, I. A. Vasalos.** Feedstock and catalyst effects in fluid catalytic cracking – Comparative yields in bench scale and pilot plant reactors. *Chem. Eng. J.*, 278 (2015) 140-149.

455. **Cruz, F.-L. M., G. N. Guzmán, J. P. O. Suárez.** Prediction of the FCC feedstocks crackability, C.T.F. *Cienc. Tecnol. Futuro*, 3 (2009) 125-142.

456. **Lerner, B. A., F. L. Himpsl.** Feed molecular properties explain cracking results. *Oil Gas J.*, 95 (1997) 61-67.

457. **Stratiev, D., R. Dinkov, I. Shishkova, E. Nikolaychuk, T. Tsaneva, M. Mitkova, S. Nenov.** Investigation on feasibility to simulate distribution of physicochemical properties and aromatics content of heavy oils employing probability distribution functions. *Erdöl Erdgas Kohle*, 131 (2015) 352-357.

458. **Stratiev, D., I. Chavdarov, E. Nikolaychuk, I. Shishkova, I. Sharafutdinov, I. Tankov, M. Mitkova.** Investigation of the fluid catalytic cracking

of different H-Oil vacuum gas oils and their blends with hydrotreated vacuum gas oil. Accepted for publication in *Pet. Sci. Technol.*, 2016.

459. **Stratiev, D., I. Shishkova, E. Nikolaychuk, I. Sharafutdinov, A. Veli, M. Mitkova, D. Yordanov, N. Rudnev.** Relationship of the aromatic structural types in vacuum gas oil to empirical correlations based on bulk properties. *Pet. Sci. Technol.*, 34 (2016) 860-865.
460. **Chavdarov, I., D. Stratiev, I. Shishkova, M. Mitkova, P. Petkov, T. Palichev.** Issues on comparing fluid catalytic cracking catalyst performance in laboratory ACE unit and commercial FCC unit. *Erdöl Erdgas Kohle*, 132 (2016) 210-214.
461. **Shishkova, I., D. Stratiev, I. Chavdarov, A. Obryvalina, R. Telyashev, M. Mitkova.** Thirty years fluid catalytic cracking in LUKOIL Neftohim Burgas - analysis of achieved progress. *Neftepererabotka i Neftehimia*, 3 (2015) 3-17(in Russian).
462. **Oliveira, L. P., D. Hudebine, D. Guillaume, J. J. Verstraete.** A review of kinetic modeling methodologies for complex processes. Oil Gas Sci. Technol. *Rev. IFP Energies nouvelles*, 71 (2016) 45.
463. **Alvarez, E., G. Marroquín, F. Trejo, G. Centeno, J. Ancheyta, J. A. I. Díaz.** Pyrolysis kinetics of atmospheric residue and its SARA fractions. *Fuel*, 90 (2011) 3602–3607.
464. **Stratiev, D.** *Dependence of fluid catalytic cracking yield distribution on process variables*. [PhD thesis]. Sofia, 28.01.2002.
465. **Stratiev, D., I. Shishkova, A. Veli, R. Nikolova, D. Stratiev, M. Mitkova, D. Yordanov.** *Fluid catalytic cracking and thermal cracking of vacuum gas oils. Effect of feedstock properties on conversion and yields*. Accepted for publication in OGEM, 2016.
466. **Sundaram, K. M. and Gllbert F. Froment.** Modeling of Thermal Cracking Kinetics. 3. Radical Mechanisms for the Pyrolysis of Simple Paraffins, Olefins, and Their Mixtures. *Ind. Eng. Chem. Fundam.*, 17 (1978) 174-182.

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