Progress in the study of the chemical kinetics of cyclic ethers in combustion

Luc-Sy Tran, Olivier Herbinet, Hans-Heinrich Carstensen, Frederique Battin-Leclerc

Université de Lille · CNRS · Université de Lorraine · Universidad Zaragoza · LRGP · araid · PC2A

Luc-Sy Tran[1], Olivier Herbinet[2], Hans-Heinrich Carstensen[3,4], Frédérique Battin-Leclerc[2]

[1] Univ. Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France
[2] Univ. Lorraine, CNRS, UMR 7274 - LRGP - Laboratoire Réactions et Génie des Procédés, F-54000, Nancy, France
[3] Fundación Agencia Aragonesa para la Investigación y Desarrollo (ARAID), Zaragoza, Spain
[4] Department of Chemical and Environmental Engineering, University of Zaragoza, Spain

For further questions, email to: luc-sy.tran@univ-lille.fr, olivier.herbinet@univ-lorraine.fr, hcarsten@unizar.es, frederique.battin-leclerc@univ-lorraine.fr

Progress in the study of the chemical kinetics of cyclic ethers (CEs) in combustion

See paper in PECS coming soon

The 2nd edition of Low-Carbon Combustion, University of Cambridge, Cambridge

Context

- Cyclic ethers (CEs) are promising biofuels produced from biomass that can help to replace traditional fossil fuels and help to mitigate global warming
- CEs are also very important products formed in the low-temperature oxidation of fuels in competition with chain-branching ketohydroperoxides.

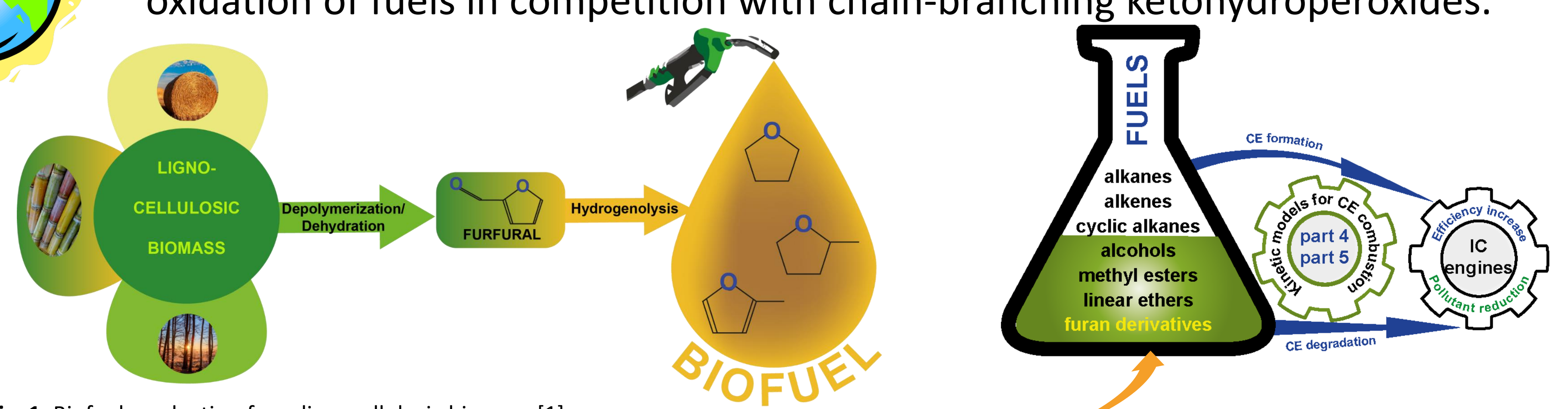

Fig. 1. Biofuel production from lignocellulosic biomass [1].

Experimental studies over the years

- 1994-2001: main focus on the formation/reactivity of saturated CEs.
- From 2012: significantly more interest in consumption chemistry.

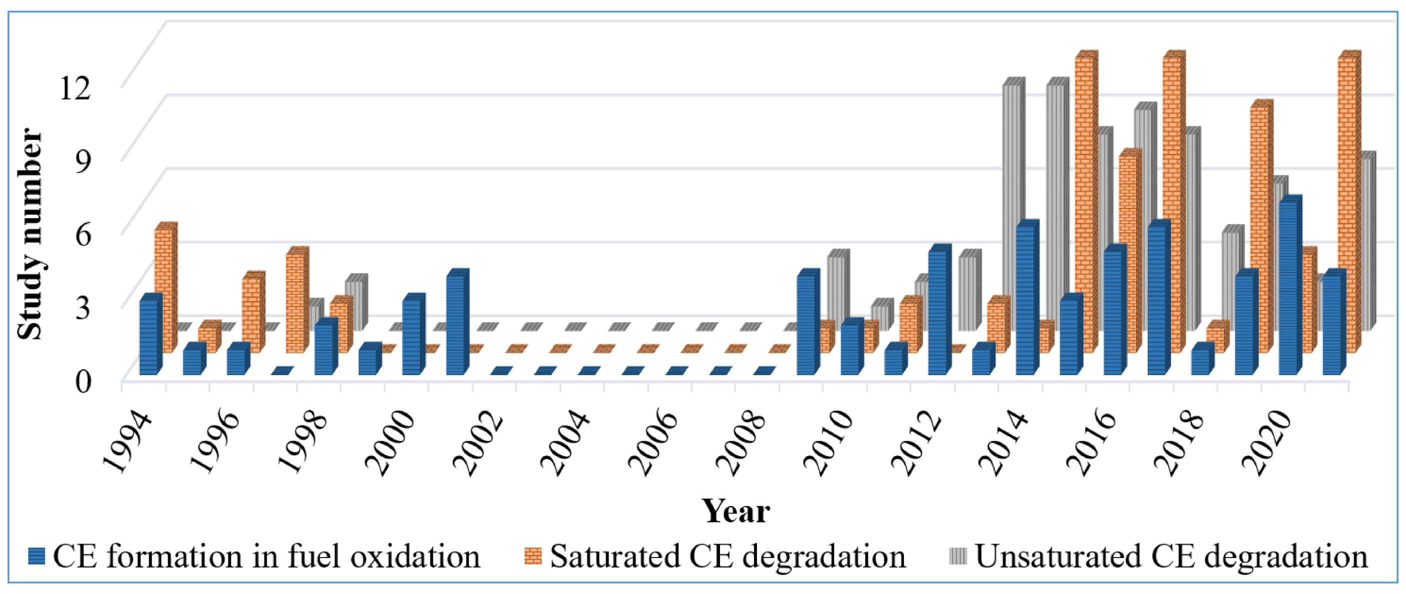

Fig. 2 Number of studies found in the literature over the years after 1994 related to CE formation during fuel low-temperature oxidation and to the consumption of saturated and unsaturated CEs [1].

Kinetic models describing CE chemistry

- Available for 14 saturated CEs (Tables 1 and 2) and for 8 unsaturated CEs (Table 3).
- Multiple models for oxirane, THF, 2-MTHF, furan, 2-MF, and 2,5-DMF, but quite limited for other CEs listed in Tables 1-3.
- No model for several CEs (*e.g.* ethyloxirane, 2-ethyltetrahydrofuran, 2-*n*-butylfuran, 2-furfurylalcohol, and 5-methylfurfural)

Table 1. Main kinetic models for the combustion of non-substituted saturated CEs.
*(Spe. N°: species number. Reac. N°: reaction number (forward). *: Conditions presented in previous rows. IDT: ignition delay time, ST: shock tube, LBV: laminar burning velocity, RCM: rapid compression machine, FR: flow reactor, PLF: premixed laminar flame)*

CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Oxirane	1990, Borisov *et al.* [2]	15	14	-IDT in ST and static reactor (T=770-1170, P=0.3-1.5) -ST pyrolysis species (T=900-1000, P=0.25-1)
	1996, Kang *et al.* [3]	30	88	-IDT in ST (T=950-1220, P=0.13(initial P), ϕ=0.5-2.0)
	1996, Würmel *et al.* [4]	30	60	-IDT in ST (T=1050-1400, P=1.9-5, ϕ=0.5-2.0)
	1996, Dagaut *et al.* [5]	67	452	-JSR species (T=800-1150, P=1-10.1, ϕ=0.5-2) -IDT in ST (T=1052-1315, P=5.1, ϕ=0.4-3.2)
	2005, Joshi *et al.* [6]	45	332	-ST pyrolysis species (T=830-1200, P=1.5-10.1)
Oxetane	1997, Dagaut *et al.* [7]	63	423	-IDT in ST (T=1050-1780, P=2-5.1, ϕ=0.5-2) -JSR species (T=800-1150, P=1-10.1, ϕ=0.5-2)
THF	1998, Dagaut *et al.* [8]	71	484	-IDT in ST (T=1000-1800, P=2-5, ϕ=0.5-2) -JSR species (T=800-1100, P=10, ϕ=0.5-1)
	2015, Tran *et al.* [9]	255	1723	-IDT in ST (T=1300-1700, P=8.1-9.3, ϕ=0.5-2) -LBV ($T_{initial}$=298-398, P=1, ϕ=0.55-1.6) -Species in PLF (P=0.07, ϕ=0.7-1.3)
	2018, Fenard *et al.* [10]	467	2390	-IDT in RCM (T=640-900, P=5-10, ϕ=1) -IDT in ST (T=830-1100, P=20-40, ϕ=1) -JSR species (T=500-1100, P=1.1, ϕ=0.5-2) & [8]* -RCM species (T=711, P=7.7) -Species in PLF [9]*
THP	1997, Dagaut *et al.* [11]	72	507	-IDT in ST (T=1000-1700, P=2-50, ϕ=0.5-2) -JSR species (T=800-1100, P=10, ϕ=0.5-2)
	2013, Labbe *et al.* [12]	125	1046	-PLF species (P=0.03, ϕ=1.75)
	2015, Tran *et al.* [13]	273	2031	- LBV ($T_{initial}$=298-398, P=1, ϕ=0.55-1.5) -IDT in ST (T=1350-1613, P=8.9-9.1, ϕ=0.5-2) -FR pyrolysis species (T=913-1133, P=1.7) & [12]*
1,3-Dioxolane	2021, Wildenberg *et al.* [14]	601	3165	-IDT in ST (T=1032-1289, P=20-40, ϕ=1) -IDT in RCM (T=662-911, P=20-40, ϕ=1) -JSR species (T=700-1180, P=10, ϕ=1)
1,4-Dioxane	2011, Yang *et al.* [15]	--	83	-ST pyrolysis species (T=1550-2100, P=0.07-0.16)

Table 2. Main kinetic models for the combustion of selected substituted saturated CEs.

CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Methyloxirane	1994, Lifshitz *et al.* [16]	37	68	-ST pyrolysis species (T=850-1250, P=2)
	2010, Burluka *et al.* [17]	127	1200	-LBV ($T_{initial}$=298, P=1, ϕ=0.7-2.1)
	2021, Ramalingam *et al.* [18]	573	3077	-LBV of [17]* -IDT in ST (T=962-1127, P=10-40, ϕ=0.5-2) (T=960-1300, P=2.5-7, ϕ=0.5-1) -IDT in RCM (T=870-980, P=10-20, ϕ=0.5-2) -ST pyrolysis species (T=900-1450, P=40) & [16]*
2,3-Dimethyloxirane	1995, Lifshitz *et al.* [19]	41	65	-ST pyrolysis species (T=900-1150, P=2)
2-MTHF	2013, Moshammer *et al.* [20]	185	1412	-PLF species (P=0.04, ϕ=1.7)
	2017, De Bruycker *et al.* [21]	412	2481	-LBV ($T_{initial}$=298-398, P=1, ϕ=0.6-1.6) -FR pyrolysis species (T=900-1100, P=1.7) -PLF species (P=0.07, ϕ=0.7-1.3) [20]*
	2017, Tripathi *et al.* [22]	250	1247	-IDT in RCM (T=639-878, P=10-40, ϕ=0.5-2) -IDT in ST (T=753-1349, P=10-20, ϕ=0.5-2) -IDT in ST (T=1050-1800, P=10.1, ϕ=1) -PLF species of [20]*
	2017, Fenard *et al.* [23]	507	2425	-IDT in RCM (T=640-900, P=30-21, ϕ=1) -IDT in ST (T=1050-1800, P=1.2-10.1, ϕ=0.5-2) -RCM species (T=719, P=7.6, ϕ=1) -PLF species of [20]*
3-MTHF	2019, Tripathi *et al.* [24]			-IDT in ST (T=715-1250, P=10-40, ϕ=0.5-2) -IDT in RCM (T=615-900, P=10-40, ϕ=0.5-2)
2,5-DMTHF	2019, Fenard *et al.* [25]	664	3197	-IDT in ST (T=860-1320, P=10-40, ϕ=1) -IDT in RCM (T=660-880, P=10-20, ϕ=1) -RCM species (T=712, P=10, ϕ=1)
2-BTHF	2017, Cai *et al.* [26]	419	1588	-LBV ($T_{initial}$=448, P=1-3, ϕ=0.7-1.35) -IDT in ST (T=705-1210, P=20, ϕ=1) -IDT in RCM (T=650-900, P=10.1, ϕ=0.5-1)
2-THFFOH	2021, Tran *et al.* [27]	479	2914	- PLF species (P=0.05, ϕ=1)
GVL	2016, De Bruycker *et al.* [28]	520	3589	-FR pyrolysis species (T=900-1100, P=1.7)
	2017, Sudholt *et al.* [29]	347	1336	-PLF species (P=0.07, ϕ=1)

Table 3. Main kinetic models for the combustion of selected unsaturated **CEs**

CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Furan	1991, Organ and Mackie [30]	-	-	-ST pyrolysis species (T=1100-1700, P=20.3)
	2000, Sendt *et al.* [31]	-	82	-ST pyrolysis species [30]*
	2011, Tian *et al.* [32]	206	1368	-PLF species (P=0.05, ϕ=1.4-2.2) -ST pyrolysis species (T=1533, P=0.26) [30]*
	2014, Liu *et al.* [33]	305	1472	-PLF species (P=0.02-0.04, ϕ=1.0-1.7) [32]*
	2017, Tran *et al.* [34]	524	3145	-FR species (T=730-1170, P=1, ϕ=0.5-2) -JSR species (T=1000-1300, P=1) -PLF species of [33]* -IDT in ST (T=1150-2010, P=1.2-16, ϕ=1)
2,3-DHF	2016, Fan *et al.* [35]	255	1723	-IDT in ST (T=1100-1635, P=1.2-10.1, ϕ=0.5-2) -ST pyrolysis species (T=900-1300, P=0.6)
	2020, Wu *et al.* [36] (used with the furan model of Tran *et al.* [34])	439	2434	-IDT in RCM (T=660-880, P=10-20, ϕ=1.0) -IDT in ST of [35]*
2,5-DHF	2016, Fan *et al.* [35]	255	1723	-IDT in ST (T=1100-1650, P=1.2-10.1, ϕ=0.5-2) -ST pyrolysis species (T=900-1080, P=1.6-6.5)
2-MF	1997, Lifshitz *et al.* [37]	36	100	-ST pyrolysis species (T=1100-1400, P=1.7-2.9)
	2013, 2014, Somers *et al.* [38, 39]	567	2889	-IDT in ST (T=1120-1800, P=1-10.7, ϕ=0.5-2) -LBV ($T_{initial}$=298-398, P=1, ϕ=0.55-1.65) -ST pyrolysis species of [37]* -PLF species (P=0.02-0.04, ϕ=1.0-1.7)
	2014, Tran *et al.* [40]	305	1472	-PLF species (P=0.02-0.04, ϕ=1.0-1.7)
	2017, Tran *et al.* [34]	524	3145	-IDT in RCM (T=737-1143, P=16-30, ϕ=1) -IDT in ST (T=1150-2010, P=1.2-16, ϕ=1) -FR species (T=730-1400, P=1, ϕ=0.02-3.33) -PLF species (P=0.02-0.04, ϕ=1.0-1.7)
	2018, Tripathi *et al.* [41]	883	4221	-IDT in RCM (T=737-1143, P=16-30, ϕ=1) -IDT in ST (T=820-2010, P=1-40, ϕ=0.25-2) -LBV ($T_{initial}$=298-398, P=1, ϕ=0.55-1.65) -PLF species (P=0.02-0.04, ϕ=0.8-1.7) -FR species (T=730-1400, P=1, ϕ=0.02-3.33)
2,5-DMF	1998, Lifshitz *et al.* [42]	50	180	-ST pyrolysis species (T=1070-1370, P=2-3.7)
	2013, Sirjean *et al.* [43]	294	1459	-IDT in ST (T=1300-1831, P=1-4, ϕ=0.5-1.5) -ST pyrolysis species of [42]*
	2013, Somers *et al.* [44]	545	2768	-IDT in ST (T=820-1800, P=1-81.1, ϕ=0.5-2) & [43]* -LBV ($T_{initial}$=298-473, P=1-7.5, ϕ=0.6-1.6) -ST pyrolysis species (T=1200-1350, P=1-2.5) & [42]* -JSR species (T=770-1220, P=10.1, ϕ=0.5-2) -FR pyrolysis species (T=873-1098, P=1.7)
	2014, Togbé *et al.* [45]	305	1472	-PLF species (P=0.02-0.04, ϕ=1.0-1.7)
	2017, Tran *et al.* [34]	524	3145	-FR species (T=730-1170, P=1, ϕ=0.5-2) -JSR species of [44]* -IDT in ST (T=1300-1900, P=1.2-16, ϕ=0.5-2) & [44]* -PLF species (P=0.02-0.04, ϕ=1.0-1.7)
2-EF	2017, Xu *et al.* [46]	568	2902	-IDT in RCM (T=766-1013, P=16-30, ϕ=0.5-2)
	2021, Song *et al.* [47]	659	3147	-FR pyrolysis species (T=846-1319, P=0.04-1)
Furfural	2021, Wang *et al.* [48]	585	3018	-FR pyrolysis species (T=929-1365, P=0.04-1) -JSR pyrolysis species (T=900-1100, P=1.07)
	2021, Jin *et al.* [49]	382	2262	-LBV ($T_{initial}$=473, P=1, ϕ=0.6-1.8) -JSR species (T=650-950, P=1, ϕ=0.4-2) -JSR pyrolysis species (T=900-1100, P=1.07)
2-MOF	2019, Yan *et al.* [50]	601	3086	-FR pyrolysis species (T=879-1107, P=1)

Examples of comparative studies on high-temperature consumption of CEs

Saturated cyclic ethers

- C–H BDE at C_2 decreases from oxirane to THF, then increases from THF to THP (Table 4).
- Ring strain energy increases from THP to oxirane (Table 4).
- Ring size and alkyl substitutions strongly affect CE reactivity (Figs. 3, 4).
- Depending on ring size, unimolecular initiation or H-abstractions (Fig. 5) will play more important role.

Table 4. Ring strain energies of non-substituted saturated CEs and their cycloalkane counterparts. Numbers in normal font on species structure: C−H BDE, in kcal/mol; those of CEs were calculated in the present work, at CBS-QB3 and at G4 (in parentheses); those of cycloalkanes were calculated at G3 by [51] and at G4 (in parentheses) by [52].

CEs		Ring strain energy (kcal/mol)	Cycloalkanes		Ring strain energy (kcal/mol)
Oxirane	104.8 (103.6)	26.80 26.52 26.3-26.4	Cyclopropane	109.2 (108.2)	27.60 27.5-27.7
Oxetane	95.5 (94.3) 101.7 (100.62)	25.70 25.30 24.7-24.9	Cyclobutane	100.5 (99.9)	26.20 26.80 25.8-26.5
THF	93.9 (92.3) 98.3 (96.8)	5.90 5.96 5.4-5.7	Cyclopentane	96.4 (95.0)	6.30 7.50 5.9-6.4
THP	96.6 (94.7) 100.9 (99) 99.5 (97.7)	0.50 0.70 0 0-1.2	Cyclohexane	100	0 (chair) 0.08 (chair) 1.0 (chair)

Influence of ring size

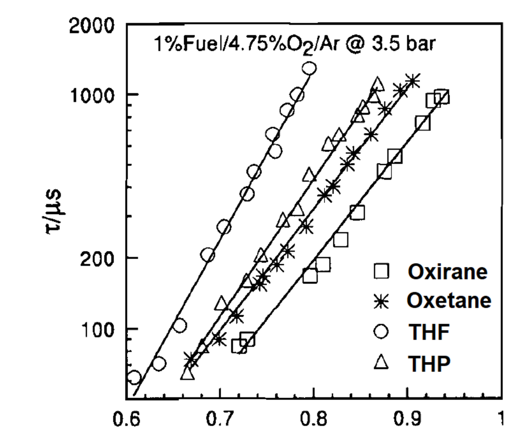

Fig. 3. Comparison of the IDTs measured in ST. Symbols: experiments with constant initial and O_2 mole fractions. Lines: trendlines. Reproduced from Ref. [8] with permission of Taylor & Francis.

Influence of alkyl substitutions

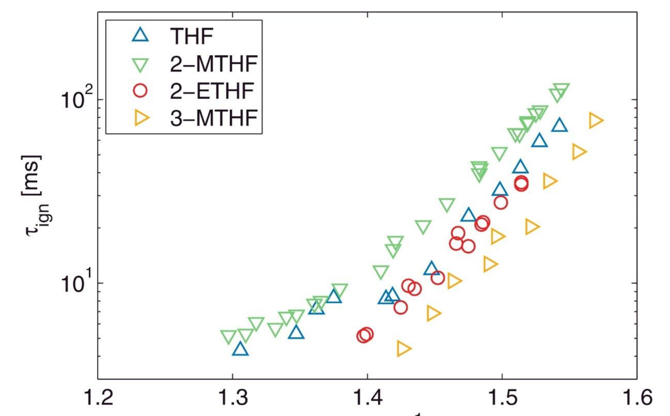

Fig. 4. IDTs of THF, 2-MTHF, 3-MTHF, 2-ETHF measured in RCM at φ=1 and 20 bar. Reproduced from Refs. [53] with permission of Elsevier.

A typical HT reaction mechanism for saturated CE (case of THP)

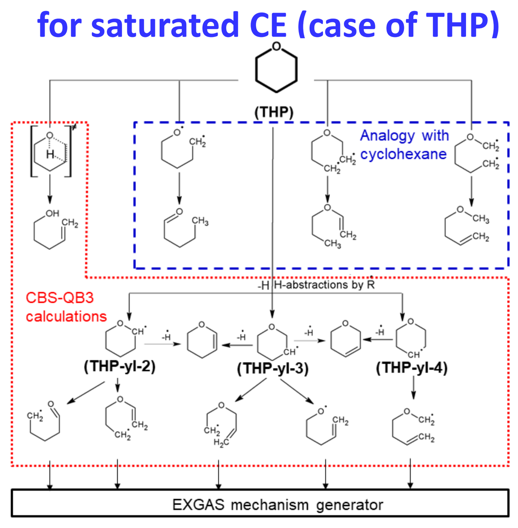

Fig. 5. Important reaction pathways and respective methods used for rate coefficient determinations in the high-temperature THP combustion model by Tran *et al.* [13].

Unsaturated cyclic ethers

Influence of the degree of unsaturation and of C_{1+} alkyl substitutions

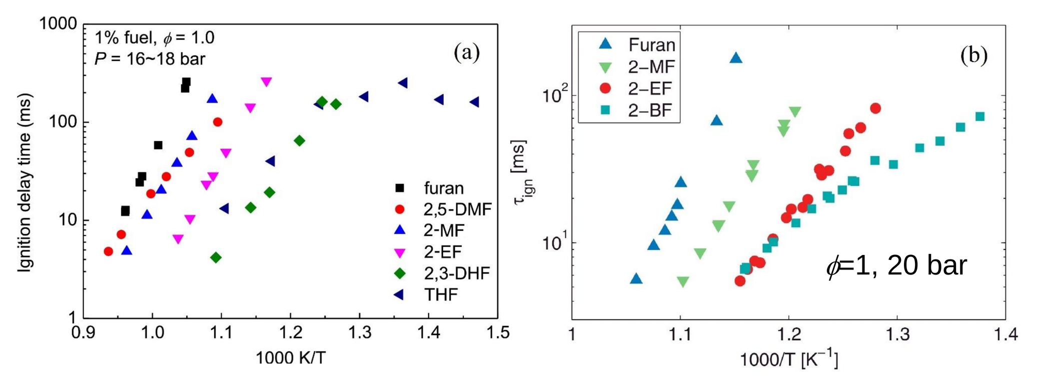

Fig. 6. IDTs of furan derivatives in RCMs. Reproduced from Ref. [36, 53] with permission of Elsevier.

Influence of oxygenated substituents

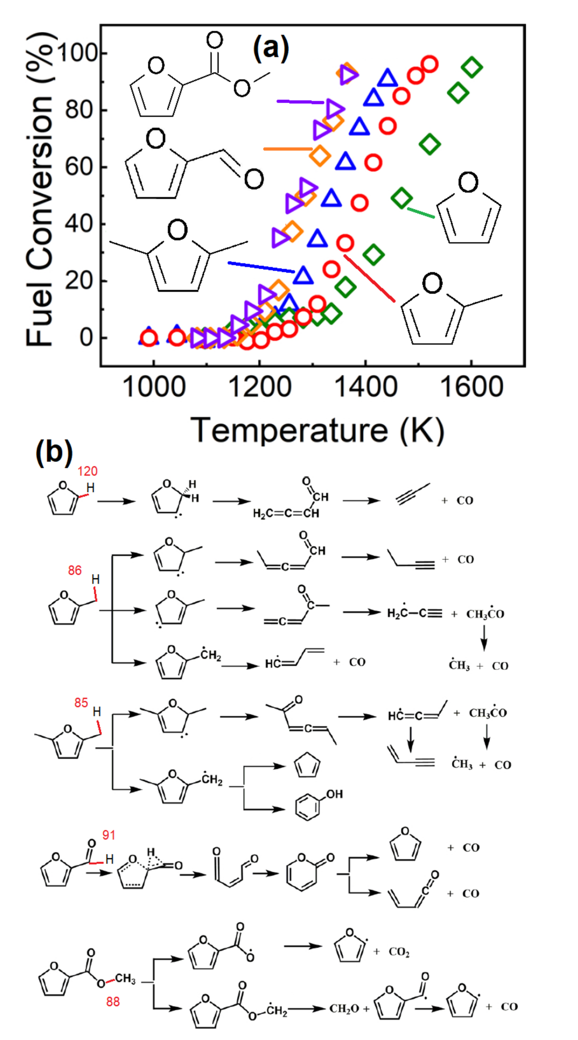

Fig. 7. Pyrolysis of substituted furans in a FR: **(a)** fuel conversion profiles (P = 0.04 bar), **(b)** major kinetic pathways. Reproduced from Ref. [48] with permission of Elsevier. The lowest BDE (kcal/mol) in each fuel is highlighted in red.

- The degree of unsaturation, alkyl or oxygenated substitutions strongly influence CE reactivity (Figs. 6, 7). This can be explained by chemical kinetics (e.g. Fig. 7b)

Species formed from furan, 2-MF, 2,5-DMF

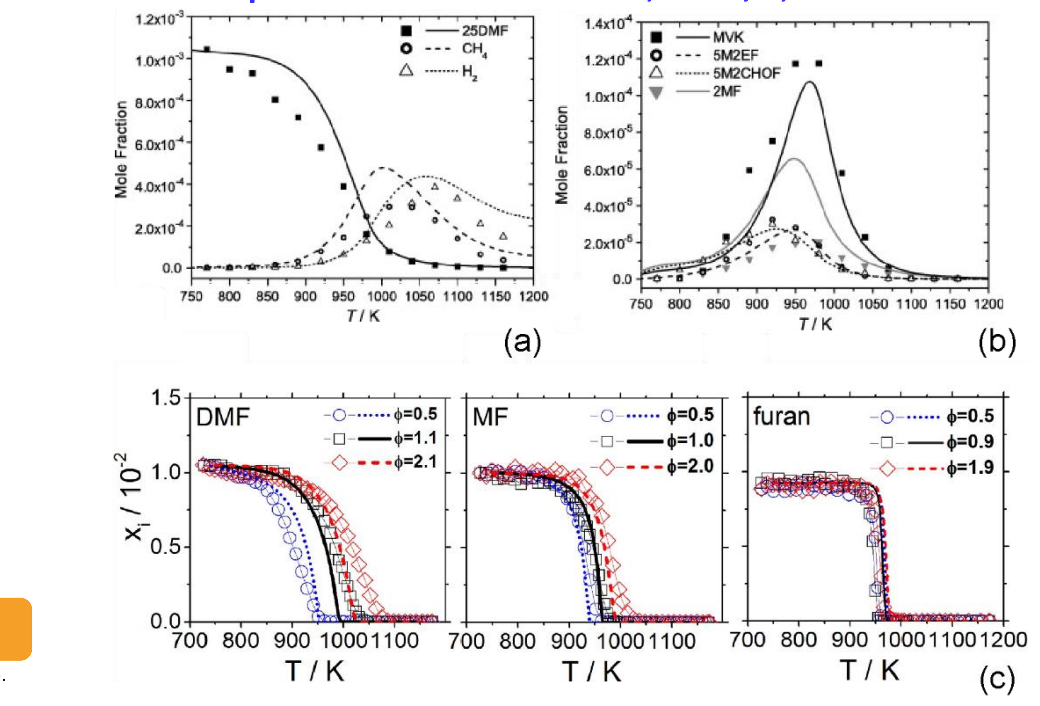

Fig. 8. Species mole fractions. **(a,b)** in 2,5-DMF oxidation (t= 0.7 s, P=10 bar, f = 1) in a JSR [44]: fuel 2,5-DMF (2,5DMF), methyl vinyl ketone (MVK), 2-ethyl-5-methylfuran (5M2EF), 5-methylfurfural (5M2CHOF); **(c)** oxidation (t~0.5-0.8 s, P=1 bar) in a FR [34]: the fuels are furan, 2-MF (MF) and 2,5-DMF (DMF). Symbols: experiments; lines: simulations. Reproduced from Ref. [34, 44] with permission of Elsevier.

- MVK, 5M2EF, 5M2CHOF are important products of 2,5-DMF oxidation.
- Strong impact of equivalence ratio ϕ on fuel reactivity seen for 2,5-DMF.

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