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

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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.

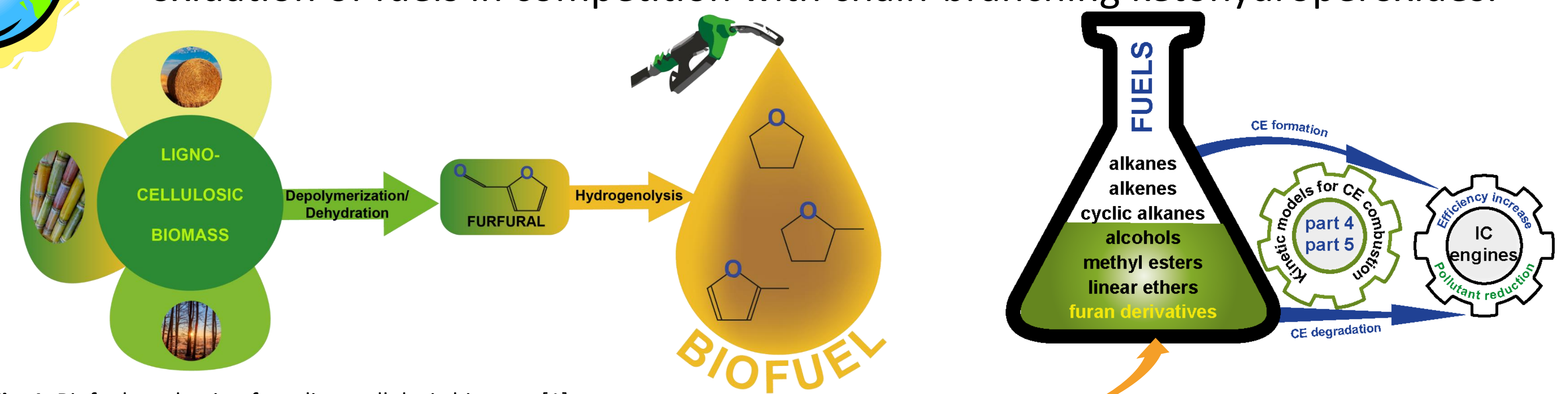


Fig. 1. Biofuel production from lignocellulosic biomass [1].

Experimental studies over the years

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

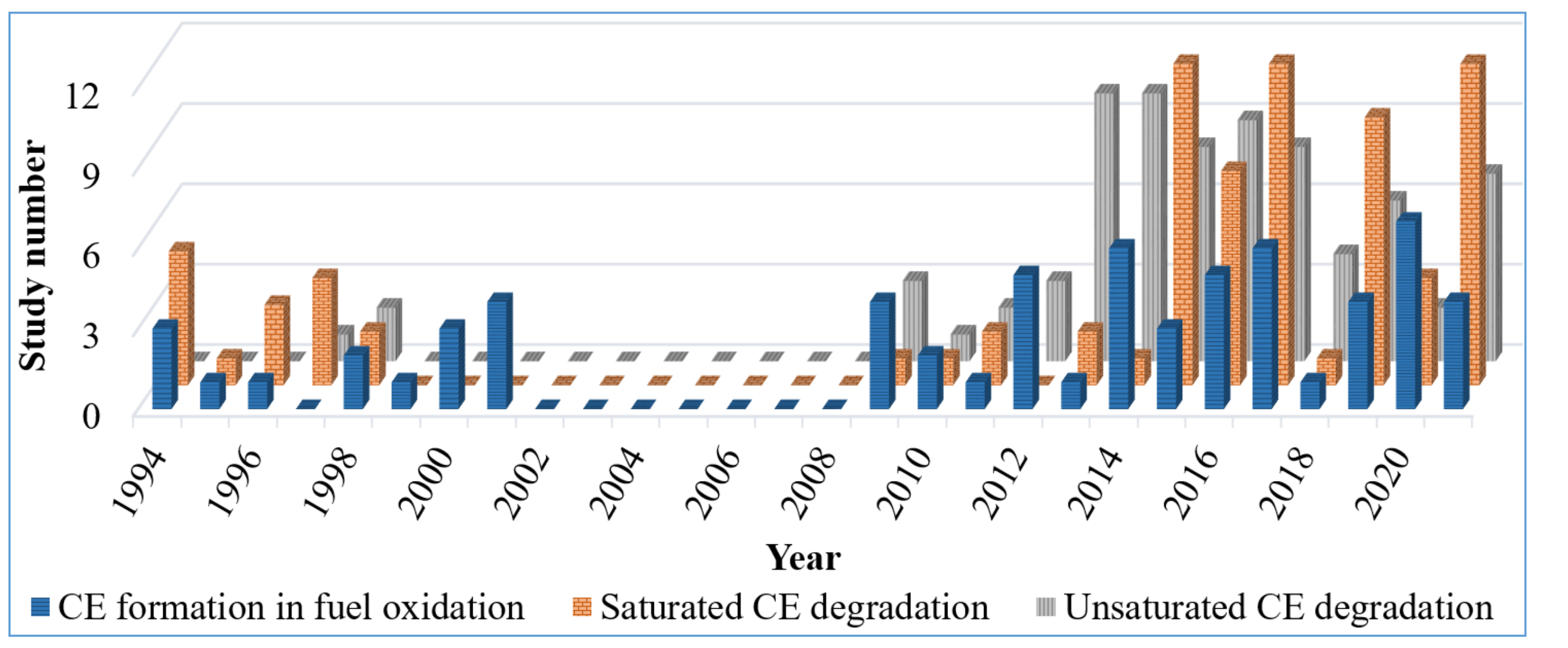


Fig. 2 Number of studies found in the literature over the years after 1994 related to CE formation during fuel low-temperature oxidation and to the consumption of saturated and unsaturated CEs [1].

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)*

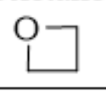
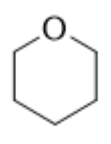
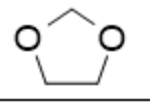
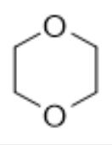
CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Oxirane 	1990, Borisov *et al.* [2]	15	14	-IDT in ST and static reactor (T=770-1170, P=0.3-1.5) -ST pyrolysis species (T=900-1000, P=0.25-1)
	1996, Kang *et al.* [3]	30	88	-IDT in ST (T=950-1220, P=0.13(initial P), ϕ=0.5-2.0)
	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.

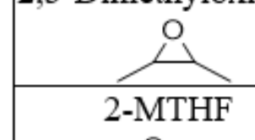
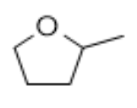
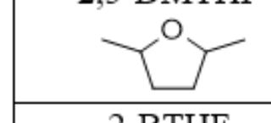
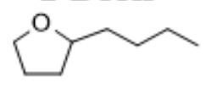
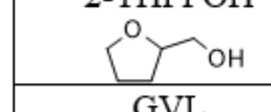
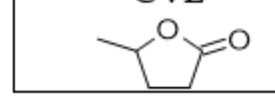
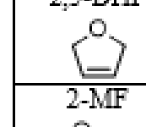
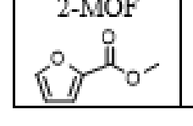
CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Methyloxirane 	1994, Lifshitz *et al.* [16]	37	68	-ST pyrolysis species (T=850-1250, P=2)
	2010, Burluka *et al.* [17]	127	1200	-LBV ($T_{initial}$=298, P=1, ϕ=0.7-2.1)
	2021, Ramalingam *et al.* [18]	573	3077	-LBV of [17]* -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**

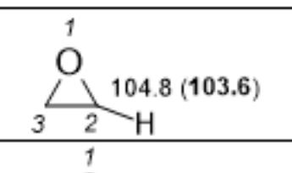
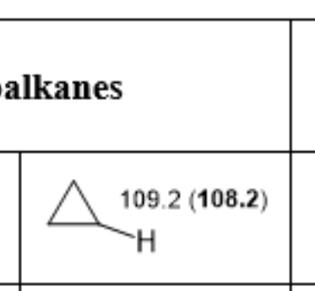
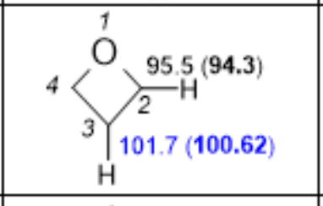
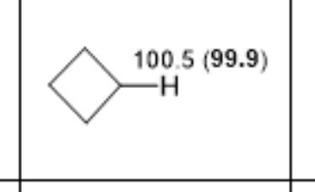
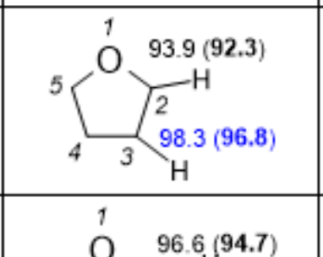
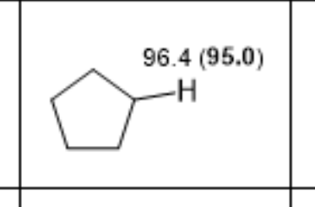
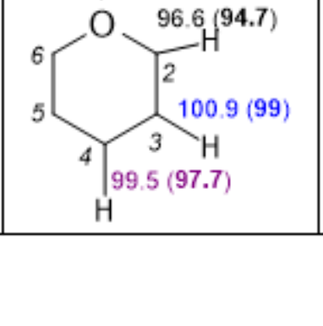
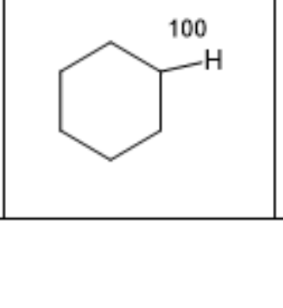
CE	Year & Ref.	Spe. N°	Reac. N°	Validation conditions *(unit: T / K, P / bar)*
Furan 	1991, Organ and Mackie [30]	-	-	-ST pyrolysis species (T=1100-1700, P=20.3)
	2000, Sendt *et al.* [31]	-	82	-ST pyrolysis species [30]*
	2011, Tian *et al.* [32]	206	1368	-PLF species (P=0.05, ϕ=1.4-2.2) -ST pyrolysis 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		26.80 26.52 26.3-26.4	Cyclopropane		27.60 27.5-27.7
Oxetane		25.70 25.30 24.7-24.9	Cyclobutane		26.20 26.80 25.8-26.5
THF		5.90 5.96 5.4-5.7	Cyclopentane		6.30 7.50 5.9-6.4
THP		0.50 0.70 0 0-1.2	Cyclohexane		0 (chair) 0.08 (chair) 1.0 (chair)

Influence of ring size

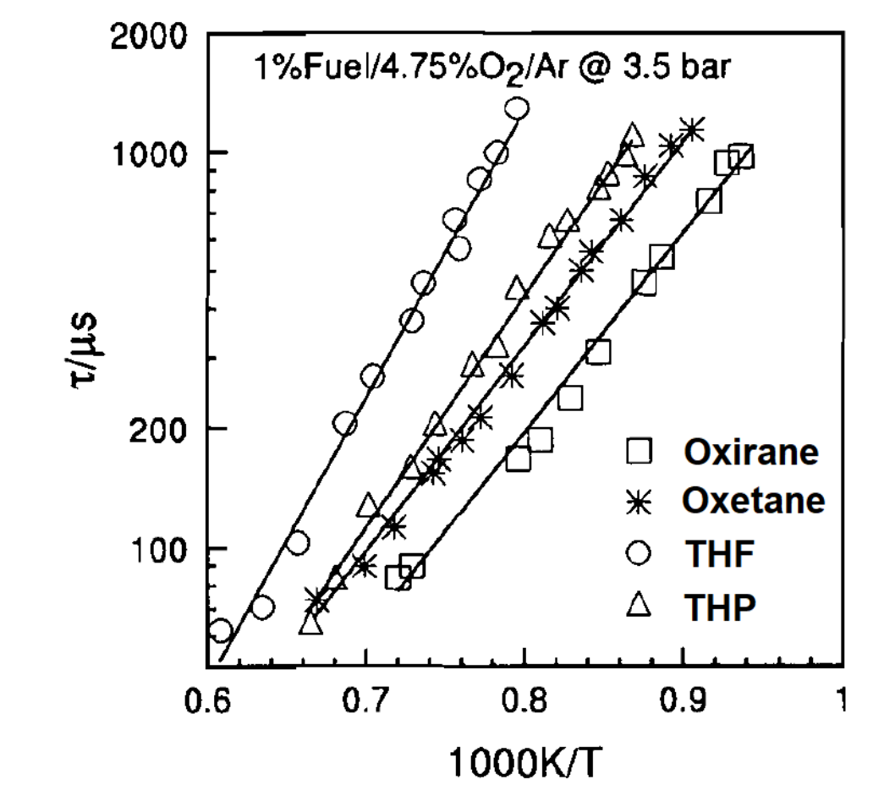


Fig. 3. Comparison of the IDTs measured in ST. Symbols: experiments with constant initial and O_2 mole fractions. Lines: trendlines. Reproduced from Ref. [8] with permission of Taylor & Francis.

Influence of alkyl substitutions

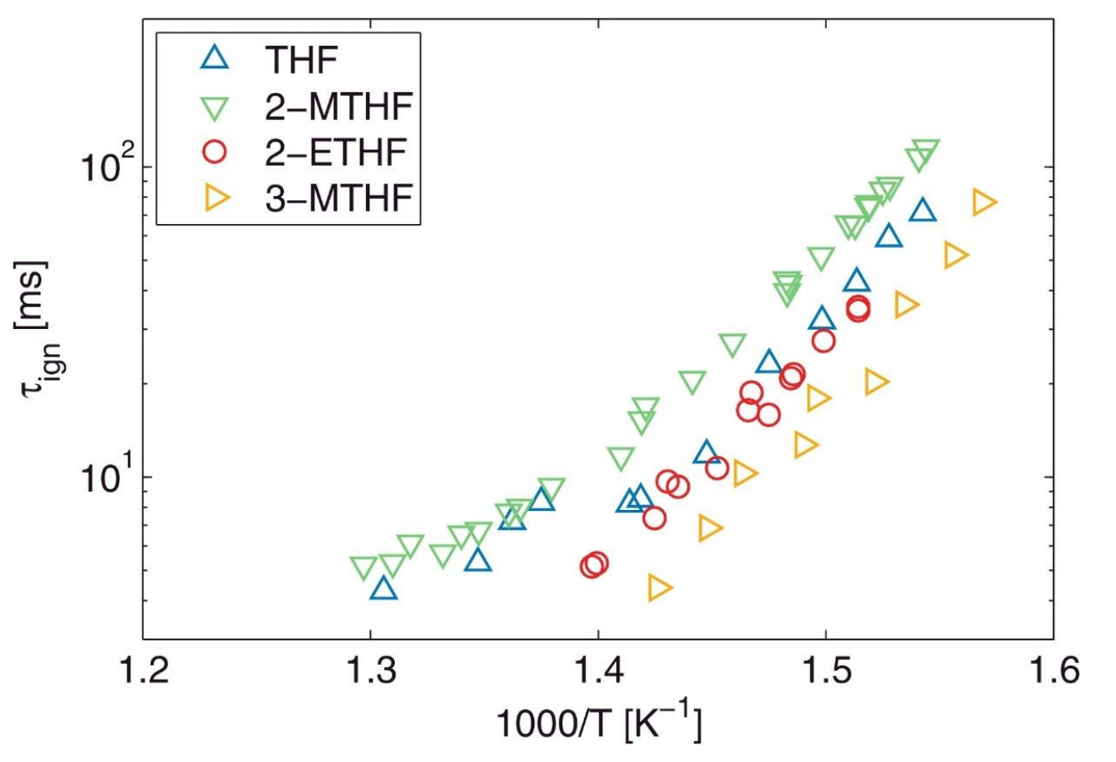


Fig. 4. IDTs of THF, 2-MTHF, 3-MTHF, 2-ETHF measured in RCM at φ=1 and 20 bar. Reproduced from Refs. [53] with permission of Elsevier.

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

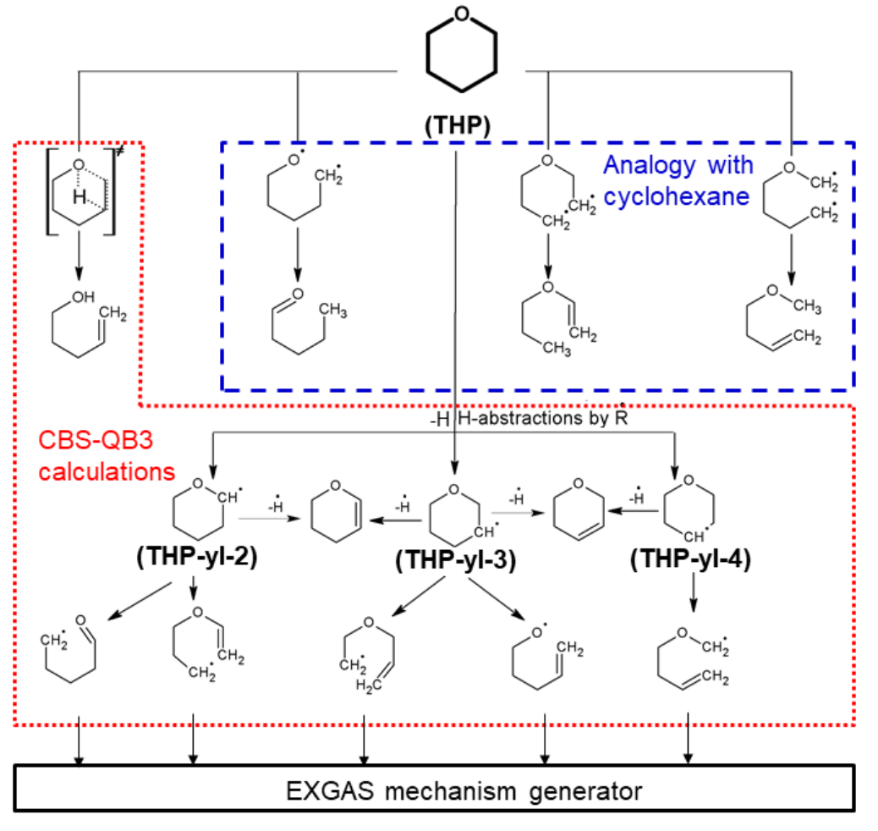


Fig. 5. Important reaction pathways and respective methods used for rate coefficient determinations in the high-temperature THP combustion model by Tran *et al.* [13].

Unsaturated cyclic ethers

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

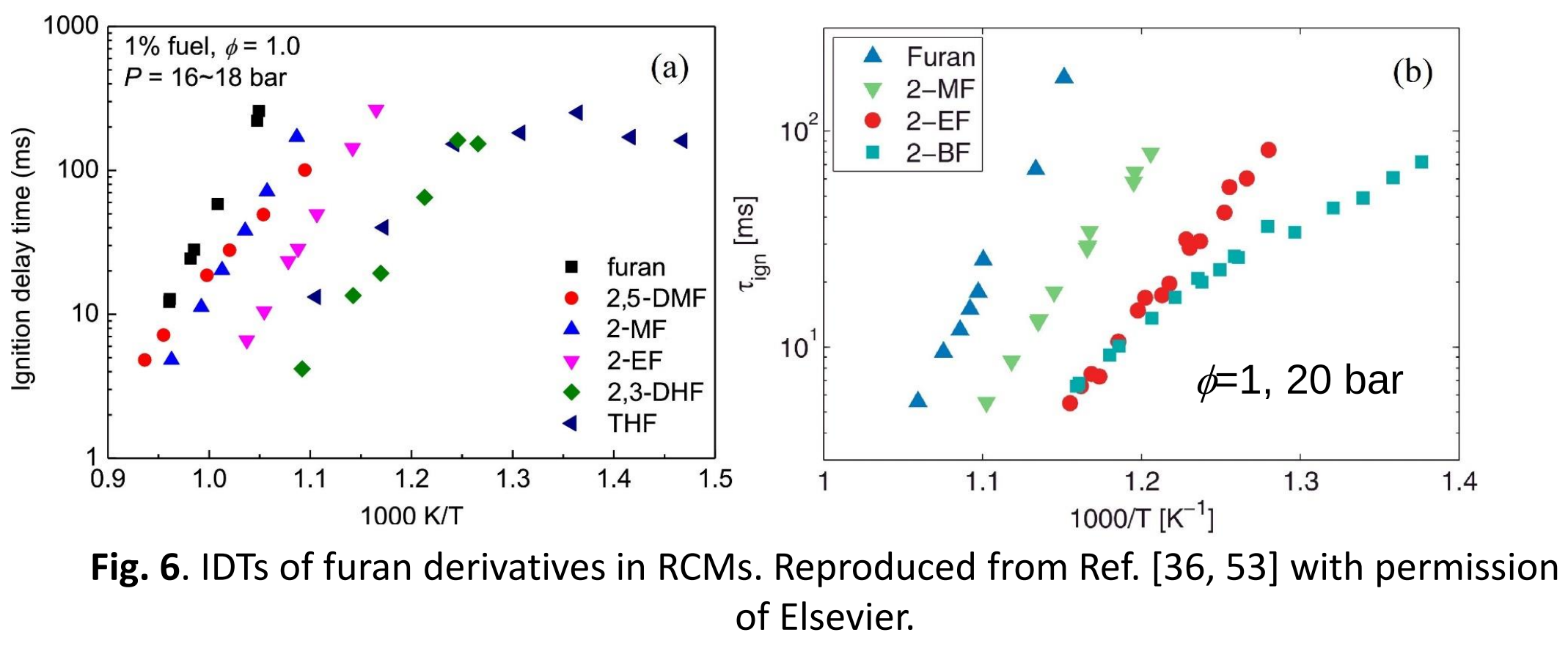


Fig. 6. IDTs of furan derivatives in RCMs. Reproduced from Ref. [36, 53] with permission of Elsevier.

- 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)

Influence of oxygenated substituents

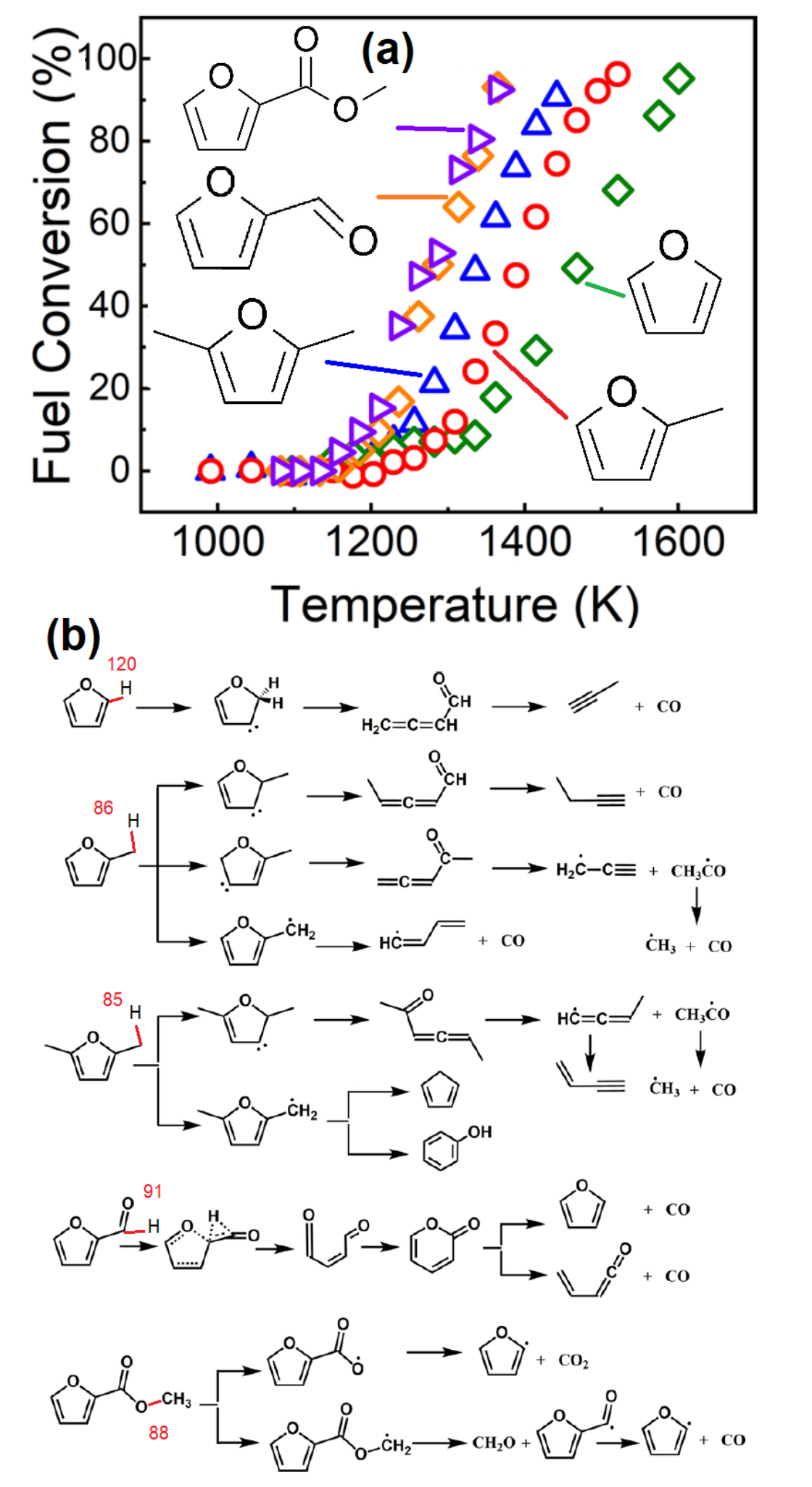


Fig. 7. Pyrolysis of substituted furans in a FR: **(a)** fuel conversion profiles (P = 0.04 bar), **(b)** major kinetic pathways. Reproduced from Ref. [48] with permission of Elsevier. The lowest BDE (kcal/mol) in each fuel is highlighted in red.

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

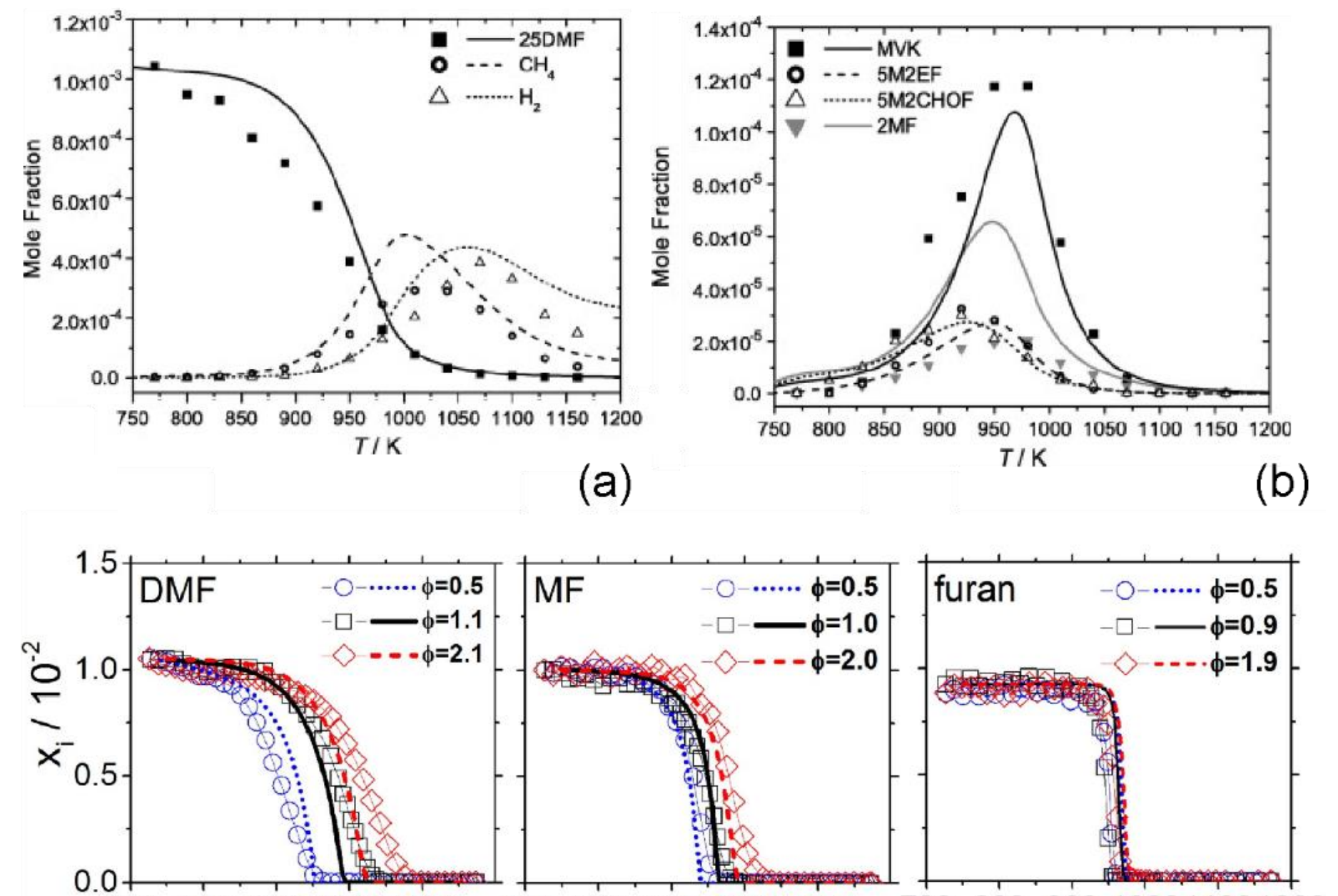


Fig. 8. Species mole fractions. **(a,b)** in 2,5-DMF oxidation (t= 0.7 s, P=10 bar, f = 1) in a JSR [44]: fuel 2,5-DMF (2,5DMF), methyl vinyl ketone (MVK), 2-ethyl-5-methylfuran (5M2EF), 5-methylfurfural (5M2CHOF); **(c)** oxidation (t~0.5-0.8 s, P=1 bar) in a FR [34]: the fuels are furan, 2-MF (MF)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