

Supporting Information

Harnessing the Potential of Biphasic Solvent Systems in Lignocellulosic Biomass Fractionation through Computational Insights

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Table S1 Review of various biphasic solvent systems used in lignocellulosic biomass fractionation, highlighting their operation condition (catalyst, temperature, time), and performance on fractionation (*i.e.*, Cellulose degradation, hemicellulose removal, and delignification).

Solvent	Biomass	Catalyst	Temperature (°C)	Time (min)	Cellulose degradation%	Hemicellulose removal %	Delignification %	References
MeTHF/H ₂ O	Bamboo	OA	120	20	36.8	48.4	24.0	1
MeTHF/ H ₂ O	Bamboo	OA	140	20	25.0	84.0	35.0	
MeTHF/ H ₂ O	Bamboo	OA	160	20	20.1	96.0	45.0	
MeTHF/ H ₂ O	Bamboo	OA	180	20	18.7	99.3	56.0	
MeTHF/ H ₂ O	Birch wood	AlCl ₃	140	60	15.0	70.0	12.5	2
MeTHF/ H ₂ O	Birch wood	AlCl ₃	150	60	28.0	85.0	41.6	
MeTHF/ H ₂ O	Birch wood	AlCl ₃	160	60	19.5	95.0	58.3	
MeTHF/ H ₂ O	Birch wood	AlCl ₃	170	60	26.7	100	66.6	
MeTHF/ H ₂ O	Birch wood	AlCl ₃	180	60	38.5	100	75.0	
MeTHF/ H ₂ O	Birch wood	FeCl ₃	180	60	32.1	100	62.5	
MeTHF/ H ₂ O	Birch wood	CuCl ₂	180	60	23.0	100	58.3	
MeTHF/ H ₂ O	Birch wood	NiCl ₂	180	60	21.2	80.0	54.1	
MeTHF/ H ₂ O	Beech wood	OA	140	180	46.6	80.5	86.4	3
MeTHF/ H ₂ O	Beech wood	FDCA	140	180	35.9	90.7	92.0	
MeTHF/ H ₂ O	Beech wood	FDCA	150	180	43.1	83.6	88.8	
MeTHF/ H ₂ O	Beech wood	FDCA	160	180	51.3	83.4	82.7	
MeTHF/ H ₂ O	Beech wood	FDCA	160	120	45.4	85.8	87.4	
MeTHF/ H ₂ O	Beech wood	FDCA	160	60	40.4	86.1	90.4	
MeTHF/ H ₂ O	empty fruit bunches (EFB)	FDCA	160	180	28.5	97.0	80.5	4
MeTHF/ H ₂ O	Bagasse	AlCl ₃	150	45	N/A	N/A	63.5	5
MeTHF/ H ₂ O	Beech wood	OA	140	180	N/A	N/A	87.0	6
MeTHF/ H ₂ O	Beech wood	OA	125	360	N/A	N/A	87.0	
MeTHF/ H ₂ O	Beech wood	OA	140	180	N/A	N/A	86.0	
MeTHF/ H ₂ O	Rice straw	OA	148	25	19.4	74.6	60.8	7
MeTHF/ H ₂ O	Rice straw	OA	125	25	22.6	52.3	63.6	

MeTHF/ H ₂ O	Rice straw	OA	125	45	1.01	58.9	16.3	
MeTHF/ H ₂ O	Rice straw	OA	125	25	16.1	55.6	71.4	
MeTHF/ H ₂ O	Rice straw	OA	125	45	15.1	60.1	42.3	
MeTHF/ H ₂ O	Rice straw	OA	160	25	42.5	64.2	53.1	
MeTHF/ H ₂ O	Rice straw	OA	160	45	27.9	65.1	25.3	
MeTHF/ H ₂ O	Rice straw	OA	160	25	23.6	85.7	55.2	
MeTHF/ H ₂ O	Rice straw	OA	160	45	25.0	88.7	46.6	
MeTHF/ H ₂ O	Wheat straw	Citric acid	120	180	8.7	34.3	26.5	
MeTHF/ H ₂ O	Wheat straw	Adipic acid	120	180	7.6	22.9	10.3	
MeTHF/ H ₂ O	Wheat straw	Fumaric acid	120	180	0.2	28.8	3.7	
MeTHF/ H ₂ O	Wheat straw	Glutaric acid	120	180	2.8	23.6	10.3	
MeTHF/ H ₂ O	Wheat straw	Tartaric acid	120	180	8.1	32.5	14.7	
MeTHF/ H ₂ O	Wheat straw	Succinic acid	120	180	7.4	26.3	9.2	
MeTHF/ H ₂ O	Wheat straw	Acetic acid	120	180	8.3	34.0	3.2	
MeTHF/ H ₂ O	Wheat straw	L-lysine	120	180	11.2	28.4	5.0	
MeTHF/ H ₂ O	Wheat straw	Acetylsalicylic acid	120	180	4.2	30.0	3.0	
MeTHF/ H ₂ O	Wheat straw	Gallic acid	120	180	2.6	30.2	0	
MeTHF/ H ₂ O	Wheat straw	Propionic acid	120	180	4.4	19.5	10.7	8
MeTHF/ H ₂ O	Wheat straw	Formic acid	120	180	6.7	24.3	13.2	
MeTHF/ H ₂ O	Wheat straw	N-butyric acid	120	180	6.2	20.7	16.0	
MeTHF/ H ₂ O	Wheat straw	Lactic acid	120	180	7.5	24.1	12.4	
MeTHF/ H ₂ O	Wheat straw	H ₂ SO ₄	120	180	8.4	68.6	42.7	
MeTHF/ H ₂ O	Wheat straw	OA	120	180	7.6	53.2	33.1	
MeTHF/ H ₂ O	Wheat straw	L-Malic acid	120	180	8.3	36.1	30.7	
MeTHF/ H ₂ O	Wheat straw	Malonic acid	120	180	3.4	27.2	12.7	
MeTHF/ H ₂ O	Wheat straw	Maleic acid	120	180	6.1	35.9	22.6	
MeTHF/ H ₂ O	Wheat straw	p-TsOH	120	180	3.7	74.9	47.6	
MeTHF/ H ₂ O	Cornstalk	H ₂ SO ₄	170	60	16.	68.1	37.5	9
MeTHF/ H ₂ O	Almond shells	H ₂ SO ₄	150	0	37.5	99.2	56.0	10

MeTHF/ H ₂ O	Beech wood	H ₂ SO ₄	145	60	N/A	N/A	70.0	11
MeTHF/ H ₂ O	Rice straw	H ₂ SO ₄	130	120	15.6	86.6	26.5	12
MeTHF/ H ₂ O	Candlenut	HCl	180	20	N/A	N/A	79.4	13
MeTHF/ H ₂ O	Rice straw	H ₂ SO ₄	110	60	20.0	76.0	17.0	14
MeTHF/ H ₂ O	Poplar wood	AlCl ₃	140	45	N/A	83.0	73.5	15
Phenoxyethanol/ H ₂ O	Rice straw	H ₂ SO ₄	130	60	17.0	87.0	60.0	16
Phenoxyethanol/ H ₂ O	Rice straw	H ₂ SO ₄	120	180	87.3	90.1	53.1	14
Phenoxyethanol/ H ₂ O	Bamboo	H ₂ SO ₄	120	60	N/A	90.0	90.0	17
Phenoxyethanol/ H ₂ O	Bamboo	H ₂ SO ₄	100	60	N/A	75.0	70.0	
Phenoxyethanol/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	110	30	2.4	61.0	30.0	18
Phenoxyethanol/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	130	70	26.6	90.0	71.5	
Phenoxyethanol/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	140	90	26.3	100	88.4	
Phenoxyethanol/ H ₂ O	Rice straw	H ₂ SO ₄	130	120	13.5	92.1	63.1	12
Phenoxyethanol/ H ₂ O	Vinegar residue	Maleic acid	120	60	14.7	53.2	48.5	19
Phenoxyethanol/ H ₂ O	Vinegar residue	Maleic acid	140	60	17.8	73.8	69.2	
Phenoxyethanol/ H ₂ O	Vinegar residue	Maleic acid	160	60	17.3	82.6	78.5	
Phenoxyethanol/H ₂ O	Rice straw	NaOH	80	30	94.9	34.1	82.1	20
Phenoxyethanol/H ₂ O	Rice straw	NaOH	55	120	92.2	40.3	78.1	
MIBK/H ₂ O	Eucalyptus	Formic acid	140	60	7.2	79.3	19.5	21
MIBK/ H ₂ O	Eucalyptus	Formic acid	160	60	23.4	97.7	35.8	
MIBK/ H ₂ O	Eucalyptus	Formic acid	180	60	42.6	98.3	43.6	
MIBK/ H ₂ O	Eucalyptus	Formic acid	200	60	64.4	100	72.6	
MIBK/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	120	50	26.6	73.38	21.1	18
MIBK/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	140	30	34.3	89.1	25.4	
MIBK/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	140	50	20.3	100	30.6	

MIBK/ H ₂ O	Amorpha fruticosa	H ₂ SO ₄	140	120	36.4	100	18.5	
MIBK/ H ₂ O	Rice straw	H ₂ SO ₄	130	120	17.1	88.1	27.7	12
MIBK/ H ₂ O	Rice straw	H ₂ SO ₄	110	60	19.0	69.0	17.0	14
MIBK/ H ₂ O	Eucalyptus	FeCl ₃	180	60	69.67	100	58.1	22
MIBK/ H ₂ O	Eucalyptus	FeCl ₃	180	60	N/A	N/A	40.3	23
MIBK/ H ₂ O	Beechwood	H ₂ SO ₄	175	60	16.2	96.6	49.4	24
MIBK/ H ₂ O	Corn stalk	Al(NO ₃) ₃ ·9H ₂ O	140	60	23.16	58.8	19.7	25
MIBK/ H ₂ O	Corn stalk	Al(NO ₃) ₃ ·9H ₂ O	160	60	33.86	90.8	20.6	
MIBK/ H ₂ O	Switchgrass	H ₂ SO ₄	170	30	N/A	77.2	23.0	26
MIBK/ H ₂ O	Switchgrass	H ₂ SO ₄	170	45	N/A	81.8	24.0	
MIBK/ H ₂ O	Switchgrass	H ₂ SO ₄	170	60	26.7	90.0	24.0	
MIBK/ H ₂ O	Eucalyptus	AlCl ₃ /DES	100	30	0.9	64.1	6.9	27
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	100	90	2.3	76.3	17.9	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	120	30	2.1	86.1	14.9	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	120	90	5.6	95.3	34.2	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	140	30	6.1	93.6	29.2	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	140	90	11.7	98.2	52.4	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	160	30	10.3	95.3	44.5	
MIBK/H ₂ O	Eucalyptus	AlCl ₃ /DES	160	90	13.4	100	66.4	
MIBK/H ₂ O	Wheat straw	CrPO ₄	180	90	N/A	88.0	N/A	28
MIBK/H ₂ O	Maple wood	H ₂ SO ₄	170	70	20.0	100	75.0	29
MIBK/H ₂ O	Corn stover	H ₂ SO ₄	170	20	N/A	98.0	N/A	30
Pentanol /H ₂ O	Poplar wood	p-TsOH	140	45	N/A	98.1	88.3	15
Pentanol /H ₂ O	Acacia Confusa wood	H ₂ SO ₄	170	60	11.0	92.0	70.2	31
Pentanol /H ₂ O	Bamboo	H ₂ SO ₄	120	30	7.17	84.47	81.5	32
Pentanol /H ₂ O	Bamboo	H ₂ SO ₄	130	20	9.04	96.2	87.8	
Pentanol /H ₂ O	Bamboo	H ₂ SO ₄	140	20	27.8	97.3	95.9	

Pentanol /H ₂ O	Sorghum bagasse	H ₂ SO ₄	180	45	28.1	90.0	74.3	33
Pentanol /H ₂ O	Aspen	H ₂ SO ₄	100	60	4.1	59.5	47.0	34
Pentanol /H ₂ O	Aspen	H ₂ SO ₄	130	60	7.2	71.0	61.4	
Pentanol /H ₂ O	Aspen	H ₂ SO ₄	160	60	8.9	85.0	91.0	
Pentanol /H ₂ O	Pine	H ₂ SO ₄	170	45	7.9	89.2	88.5	35
Pentanol /H ₂ O	Wheat straw	H ₂ SO ₄	170	45	5.5	93.3	89.7	
Pentanol /H ₂ O	Aspen	p-TsOH	80	40	N/A	39.0	33.0	36
Pentanol /H ₂ O	Aspen	p-TsOH	100	40	N/A	67.0	63.0	
Pentanol /H ₂ O	Aspen	p-TsOH	120	40	4.2	98.2	85.5	
Pentanol /H ₂ O	Aspen	p-TsOH	140	40	N/A	97.0	90.0	
Pentanol /H ₂ O	Aspen	p-TsOH	160	40	N/A	95.0	92.0	
Pentanol /H ₂ O	Poplar	p-TsOH/mannitol	120	40	7.0	95.1	92.8	37
Butanol/H ₂ O	Eucalyptus	H ₂ SO ₄	180	45	17.0	64.7	72.0	38
Butanol/H ₂ O	Sorghum bagasse	H ₂ SO ₄	200	60	2.0	90.0	78.0	39
Butanol/H ₂ O	Sorghum bagasse	H ₂ SO ₄	180	45	8.9	93.0	64.7	33
Butanol/H ₂ O	Sorghum bagasse	H ₂ SO ₄	200	120	19.0	63.0	58.0	40
Butanol/H ₂ O	Vine shoots	H ₂ SO ₄	190	20	15.3	98.0	67.8	41
Butanol/H ₂ O	Wheat straw	H ₂ SO ₄	160	20	9.8	93.5	62.0	42
Butanol/H ₂ O	Beech wood	H ₂ SO ₄	175	120	0.1	73.6	97.0	43
Butanol/H ₂ O	Pinus pinaster wood	H ₂ SO ₄	190	10	13.0	97.0	92.4	44
Butanol/H ₂ O	Poplar wood	H ₂ SO ₄	140	45	N/A	97.2	77.9	15
Butanol/H ₂ O	Arundo donax	H ₂ SO ₄	180	20	22.7	95.2	85.0	45
Butanol/H ₂ O	Arundo donax	H ₂ SO ₄	180	20	33.3	97.9	86.7	
Butanol/H ₂ O	Druff	HCl	(reflux)	360	N/A	68.4	N/A	46

Table S2 The review of enzymatic hydrolysis conversion of solid residue of biphasic solvent system pretreatment.

Solvent	Acid Catalyst	Temperature (°C)	Time (min)	Time(h)	Solid loading (%)	Enzyme	Enzymatic hydrolysis conversion (%)		References
MeTHF/ H ₂ O	OA	120	20	96	2%	20 FPU/g endoglucanases, exoglucanases, β -glucosidases	20.4		1
MeTHF/ H ₂ O	OA	140	20				50.0		
MeTHF/ H ₂ O	OA	160	20				89.0		
MeTHF/ H ₂ O	OA	180	20				92.9		
MeTHF/ H ₂ O	AlCl ₃	140	60	72	2%	15 FPU/g cellulase	12.0		2
MeTHF/ H ₂ O	AlCl ₃	150	60				15.5		
MeTHF/ H ₂ O	AlCl ₃	160	60				23.0		
MeTHF/H ₂ O	AlCl ₃	170	60				49.0		
MeTHF/ H ₂ O	AlCl ₃	180	60				77.0		
MeTHF/ H ₂ O	FeCl ₃	180	60				41.0		
MeTHF/ H ₂ O	CuCl ₂	180	60				46.0		
MeTHF/ H ₂ O	NiCl ₂	180	60				56.0		
MeTHF/ H ₂ O	OA	140	180	72	2%	60 FPU/g Accellerase® 1500	23.0		3
MeTHF/ H ₂ O	FDCA	140	180				13.0		
MeTHF/ H ₂ O	FDCA	150	180				26.0		
MeTHF/ H ₂ O	FDCA	160	180				46.0		
MeTHF/ H ₂ O	FDCA	160	120				34.0		
MeTHF/ H ₂ O	FDCA	160	60				19.0		
MeTHF/ H ₂ O	FDCA	160	180	72	2%	60 FPU/g Accellerase® 1500	73.0		4
MeTHF/ H ₂ O	AlCl ₃	150	45	96	2.5%	β -glucosidases, cellulase	5 FPU	46.4	5
							10 FPU	58.4	
							15 FPU	68.8	
							30 FPU	89.3	
MeTHF/ H ₂ O	OA	148	25	72	6%	15 FPU/g, cellulase, β -glucosidases,	42.7		7

MeTHF/ H ₂ O	OA	125	25		6%		59.0	
					8%		38.0	
MeTHF/ H ₂ O	OA	125	45		6%		41.0	
					8%		31.0	
MeTHF/ H ₂ O	OA	125	25		6%		45.0	
					8%		37.0	
MeTHF/ H ₂ O	OA	125	45		6%		44.0	
					8%		30.0	
MeTHF/ H ₂ O	OA	160	25		6%		79.0	
					8%		31.0	
MeTHF/ H ₂ O	OA	160	45		6%		75.0	
					8%		40.0	
MeTHF/ H ₂ O	OA	160	25		6%		74.0	
					8%		48.0	
MeTHF/ H ₂ O	OA	160	45		6%		73.0	
					8%		39.0	
MeTHF/ H ₂ O	p-TsOH	100	180	72	2%	20 FPU/g, cellulase	68.9	8
		120					84.0	
		140					95.5	
		160					97.0	
		180					99.4	
MeTHF/ H ₂ O	H ₂ SO ₄	170	60	72	2%	15 FPU/g, cellulases	78.9	9
Phenoxyethanol/ H ₂ O	H ₂ SO ₄	120	180	72	2.5%	20 FPU/g cellulases	88.0	14
Phenoxyethanol/ H ₂ O	H ₂ SO ₄	120	60	72	5%	10 FPU/g cellulases	79.2	17
Phenoxyethanol/ H ₂ O	H ₂ SO ₄	100	60				30.7	
Phenoxyethanol/ H ₂ O	H ₂ SO ₄	130	120	72	2%	191.7 FPU/g, cellulases	87.0	12
Phenoxyethanol/ H ₂ O	Maleic acid	120	60	72	2%	15 FPU/g cellulases	46.0	19
Phenoxyethanol/ H ₂ O	Maleic acid	140	60				72.0	
Phenoxyethanol/ H ₂ O	Maleic acid	160	60				82.7	
Phenoxyethanol/ H ₂ O	NaOH	80	30	72	2.5%	20 FPU/g cellulases	82.5	20
Phenoxyethanol/ H ₂ O	NaOH	55	120				80.0	

MIBK/H ₂ O	Formic acid	140	60	72	2%	17 FPU/g cellulase	25.0		21
MIBK/ H ₂ O	Formic acid	160	60				32.0		
MIBK/ H ₂ O	Formic acid	180	60				70.0		
MIBK/ H ₂ O	Formic acid	200	60				78.0		
MIBK/ H ₂ O	FeCl ₃	180	60	36	1%	20 FPU/g Cellulase (endoglucanases, β-glucosidases and exoglucanases)	87.0		22
MIBK/ H ₂ O	H ₂ SO ₄	175	60	24	2%	8.4 mg/g Cellic® CTec2	70.0		24
MIBK/ H ₂ O	Al (NO ₃) ₃ ·9H ₂ O	140	60	72	2%	20 FPU/g, cellulase	66.0		25
MIBK/ H ₂ O	Al (NO ₃) ₃ ·9H ₂ O	160	60				85.5		
MIBK/H ₂ O	H ₂ SO ₄	170	60	48	2%	20 mg/g Cellic® CTec2	73.3		26
MIBK/ H ₂ O	AlCl ₃ /DES	100	90	72	2%	15 FPU/g, cellulase	30.3		27
MIBK/ H ₂ O		120					57.3		
MIBK/ H ₂ O		140					80.8		
MIBK/ H ₂ O		160					77.0		
Pentanol /H ₂ O	H ₂ SO ₄	170	60	72	2%	15 FPU/g cellulase (CellicCtec-2)	92.1		31
Pentanol / H ₂ O	H ₂ SO ₄	120	30	72	2%	20 FPU/g cellulase	92.6		32
Pentanol /H ₂ O	H ₂ SO ₄	180	45	72	2%	Cellic CTec2	90.0		33
Pentanol /H ₂ O	H ₂ SO ₄	160	60	72	10	15 FPU/g Cellic CTec2	96.0		34
Butanol /H ₂ O							82.0		
Ethanol /H ₂ O							50.0		
Dioxane/ H ₂ O							55.0		
Pentanol /H ₂ O	H ₂ SO ₄	170	45	72	10	15 FPU/g Cellic CTec2	93.3		35
Pentanol /H ₂ O	H ₂ SO ₄	170	45				88.6		
Pentanol /H ₂ O	p-TsOH	80	40	72	N/A	Cellic CTec2	10 FPU	22.0	36
							15 FPU	28.0	
Pentanol /H ₂ O	p-TsOH	100	40				10 FPU	49.0	
							15 FPU	61.0	
Pentanol /H ₂ O	p-TsOH	120	40				10 FPU	73.2	
				15 FPU	95.3				

Pentanol /H ₂ O	p-TsOH	140	40				10 FPU	77.0	
							15 FPU	98.0	
Pentanol /H ₂ O	p-TsOH	160	40				10 FPU	76.0	
							15 FPU	98.2	
Pentanol /H ₂ O	p-TsOH	180	40				10 FPU	78.0	
							15 FPU	98.1	
Pentanol /H ₂ O	p-TsOH/1% mannitol	120	40	72	10	7.5 FPU/g Cellic CTec2	73.3		37
Pentanol /H ₂ O	p-TsOH/5% mannitol						94.5		
Pentanol /H ₂ O	p-TsOH/10% mannitol						95.4		
Pentanol /H ₂ O	p-TsOH/15% mannitol						96.5		
Pentanol /H ₂ O	p-TsOH						65.3		
Butanol/H ₂ O	H ₂ SO ₄	180	45	72	10	Cellic CTec2	96.0		38
Butanol/H ₂ O	H ₂ SO ₄	200	60	72	2%	cellulase	2.5	44.0	39
							5	76.0	
							7.5	93.0	
							10	98.0	
Butanol/H ₂ O	H ₂ SO ₄	180	45	72	2%	Cellic CTec2	78.0		33
Butanol/H ₂ O	H ₂ SO ₄	160	20	72	13%	84 FPU Cellic CTec2	89.0		42
Butanol/H ₂ O	H ₂ SO ₄	175	120	72	9%	9.6 FPU Cellic CTec2	75.3		43
			60				71.7		
		160	120				76.9		
			60				54.8		
		150	120				49.8		
			60				24.7		
Butanol/H ₂ O	H ₂ SO ₄	190	10	72	10%	Cellic Ctec3	20 FPU	95.0	44

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