

Supporting information

Sustainable and efficient production of furoic acid from furfural through amine assisted oxidation with hydrogen peroxide and its implementation for the synthesis of alkyl furoate

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S1. Experimental method

Materials

Furfural (98 %), hydrogen peroxide (30 and 50 %), 1-dodecanol (98 %) was bought from Merck. NaOH and H₂SO₄ (66.6 %) were bought from VWR. Tributyl amine was bought from TCI.

Oxidation of furfural into furoic acid

Furfural (5 g, 1 eq, 52 mmol) and tributyl amine (9.6 g, 1 eq, 52 mmol) were loaded in a 25 ml round bottom flask equipped with a thermometer. 30 % hydrogen peroxide (5.9 g, 1 eq, 52 mmol) were weighted in a syringe and slowly injected in the reaction flask. In case 50 % of hydrogen peroxide was used 3.54 g were used. The addition was regulated so that the temperature doesn't overshoot the set-point by 15 °C. Experiments were replicated in triplicate with standard deviation less than 5%. Product analysis was carried through HPLC.

In larger scale 25 g of furfural were used and amounts scaled accordingly. The addition of 50 % hydrogen peroxide was carried to guarantee that reaction temperature doesn't exceed the set-point. Product analysis was done using HPLC to quantify the furoic acid and NMR to quantify the amine oxide formed. Experiments were replicated in triplicate with standard deviation less than 5 %.

Isolation of furoic acid from the reaction mixture

To a large-scale reaction batch containing 29 g of furoic acid, 44.4 g amine content and 16.2 g of water (derived from the reaction of 1.3 hydrogen peroxide with furfural), was added slowly 52 g of 20% NaOH solution and stirred for 10 min. The mixture was transferred into a separating funnel and the upper amine layer was separated. The water layer was washed with 3*60 ml of ethyl acetate to remove amine oxide. The water layer was adjusted to pH 1 using 66.6 % H₂SO₄ solution. Furoic acid precipitated as white powder (81 %) yield and separated through vacuum filtration.

Esterification of furoic acid with dodecanol

The esterification was repeated with same procedure as reported in our previous publication.¹ The isolated furoic acid (25 g) were dissolved in 100 ml of acetonitrile and filtered to remove the residual sodium sulphate. Acetonitrile was removed through rotoevaporation and furoic acid recovered as white powder. Furoic acid (23 g, 0.205 mol) and dodecanol (39 g, 0.205 mol) were mixed and heated at 160 °C in a round bottom flask at atmospheric pressure. When complete dissolution of furoic acid arises 1 % of H₂SO₄ (respect the reactant) was introduced and the reaction left for 1 h. The product was analysed by NMR.

Implementation of compounds in Aspen Plus

Quantum chemical calculations to create the chemical structure of the compounds was done using TURBOMOLE v7.02 (with TmoleX v4.5.2. graphic interface) software. Molecular structures of the compounds were optimized until its minimum energy level. After that, quantum chemical calculations were carried out to generate a COSMO file. The standard method used in COSMOtherm is B88-P86 (bp) functional and TZVP basis with RI approximation using COSMO solvation model. Through these quantum chemical calculations, a COSMO file was created containing energies, geometries and polarization charge of the σ -surface.

COSMO-RS method program package (version C30_1904) and its parametrization BP_TZVP_C30_19 was used in COSMOtherm software. COSMO-RS method was used to create pseudocomponents into Aspen Properties. COSMOtherm was used to complete the normal boiling point (NBP), density, σ -profile and COSMO-volume calculations (the last two to use the COSMOSAC model from Aspen Properties).

To implement ILs into ASPEN PLUS v11 simulator, a property package was created in Aspen Properties v11. Compounds were defined as pseudocomponents. Normal boiling point, density and molecular weight was the required information imported from COSMOtherm needed to create the pseudocomponent. COSMOSAC model was selected as thermodynamic model and gamma method was modified to use COSMOSAC-Mathias modification. σ -profile was specified as pure component properties SGPRF1-5 and COSMO-volume as CSACVL component parameter [4].

Process simulation

Process simulation was done using Aspen Plus v11 operating cost were evaluated using values reported in our previous publication² and herein reported.

Table S 1 Price to estimate the operating cost of the plant

	Cost
Furfural	2 \$/Kg
Dodecanol	2 \$/Kg
Cost of fuel (natural gas)	2.74 \$/GJ
Steam (for heating)	0.11 \$/Kg
Cooling water	0.06 \$/m ³
Primary waste water treatment	0.03 \$/m ³
Hydrogen Peroxide (dry base)	0.6 \$/Kg
Tributyl amine	2 \$/Kg
H ₂ SO ₄ (dry basis)	0.2 \$/Kg
NaOH (dry basis)	0.4 \$/Kg
Ethyl acetate	2 \$/Kg

CO₂ emissions were evaluated through the heating requirements and burning of organic solvents. CO₂ emissions from heating requirements were evaluated considering a thermal efficiency of 0.8 and natural gas requirement calculated accordingly.

Capital cost were evaluated through Aspen plus economics which estimate the purchase cost and installed costs. Reactor sizing were done by implementing the residence time of the reaction (4 h oxidation, 2 h esterification, 10 min acid base reactions). Other operating costs and capital costs were estimated through factor of the total installed costs according to the following table reported in typical chemical engineering books.³

Table S 2 Factor of the total installed cost to evaluate the annual operating costs.

Maintenance	0.1
Laboratory cost	0.2
Supervision	0.2
Plant overhead	0.5
Depreciation	0.1
Insurance	0.01
Local tax	0.02
Royalties	0.01

Table S 3 Parameters to estimate capital cost

Direct field cost (DF)	Sum of installed cost
Direct field labour cost (DFL)	0.25*DF
Indirect field cost (IF)	1.15* DFL
Total field cost (TFC)	DF+DFL+IF
Home office cost (HOC)	0.3*DF
Other project cost (OPC)	0.03*DF+0.15*(TFC+HOC)
Total Project cost	TFC+HOC+OPC

Labour was evaluated by estimating the number of operators according the following correlation by Alkhayat and Gerrard⁴

$$Nop = (6.29 + 31.7P^2 + 0.23Nnp)^2$$

Where P are the number of units handling the solids and Nnp handling liquids. For each operator is estimated a salary of 70.000 \$/year.

Total operating cost are estimated by annualizing the total and installed cost over 10 years, operating cost to run the plant (utilities, auxiliaries, feedstock), labour and the other operating cost to run the plant listed in Table S 2.

Minimum selling price is calculated as the ratio of the productivity of the plant divided by the total operating cost.

Results

Oxidation and separation

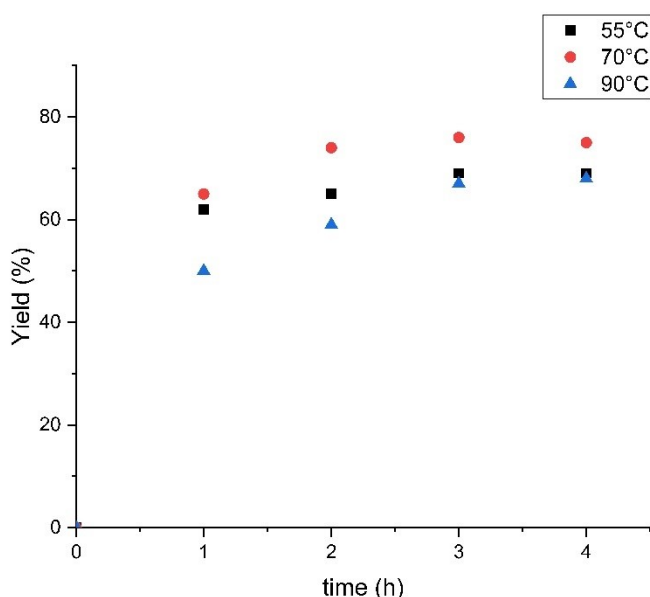


Figure S 1 Kinetic analysis of the oxidation of furfural into furoic acid upon the addition of 1 eq of H₂O₂ in large scale batch



Figure S 2 Isolation of furoic acid. On the left with residual furfural (10 %) and on the right with complete furfural conversion.

Process simulation

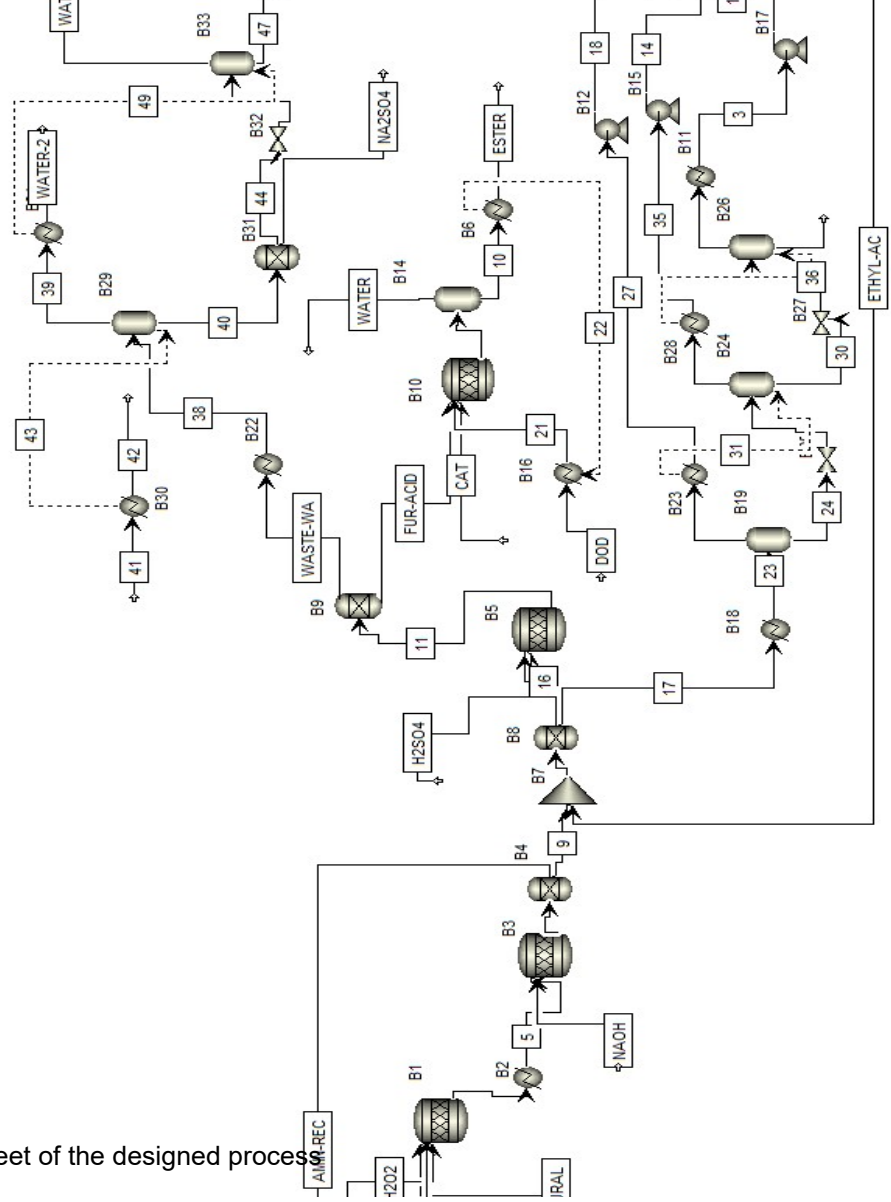


Figure S 3 Complete process flowsheet of the designed process

Table S 4 Flow rate of the most significant streams in the flowsheet (Kg/h)

	AMIN-REC	AMINE-ML CAT	DOD	EA-MU	ESTER	ETHYL-AC	FA	FUR-ACID	FURFURAL	H2O2	H2SO4	NA2SO4	NA2SO4-2	NAOH	WASTE-WA	WATER	WATER-2	WATER-3		
	1638	289	10	1938	239	3046	4232	25	1559	999	919	1020	339	483	2081	3382	461	1451	1084	
FURFURAL	0	0	0	0	0	0	0	0	999	0	0	0	0	0	0	0	0	0	0	0
FUROICAC	0	0	0	0	0	0	0	0	1049	0	0	0	0	45	0	0	0	3	0	0
NAFURAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NBU3	1638	289	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NOBU3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2O2	0	0	0	0	0	0	43	0	0	460	0	0	0	0	0	0	0	0	0	0
ETHYLAC	0	0	0	0	239	0	4189	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4	0	0	10	0	0	520	0	510	0	0	1020	0	0	0	0	0	0	0	0	0
NAOH	0	0	0	0	0	0	0	0	0	0	0	0	0	416	0	0	0	0	0	0
NA2SO4	0	0	0	0	0	0	0	25	0	0	0	339	375	0	739	0	0	0	0	0
DODECNOL	0	0	0	1938	0	193	0	0	0	0	0	0	0	0	0	1	0	0	0	0
DODECFUR	0	0	0	0	0	2257	0	0	0	0	0	0	0	0	0	368	0	0	0	0
WATER	0	0	0	0	0	76	0	0	0	459	0	0	63	1665	2526	93	1448	1015	0	0

Furoic acid production

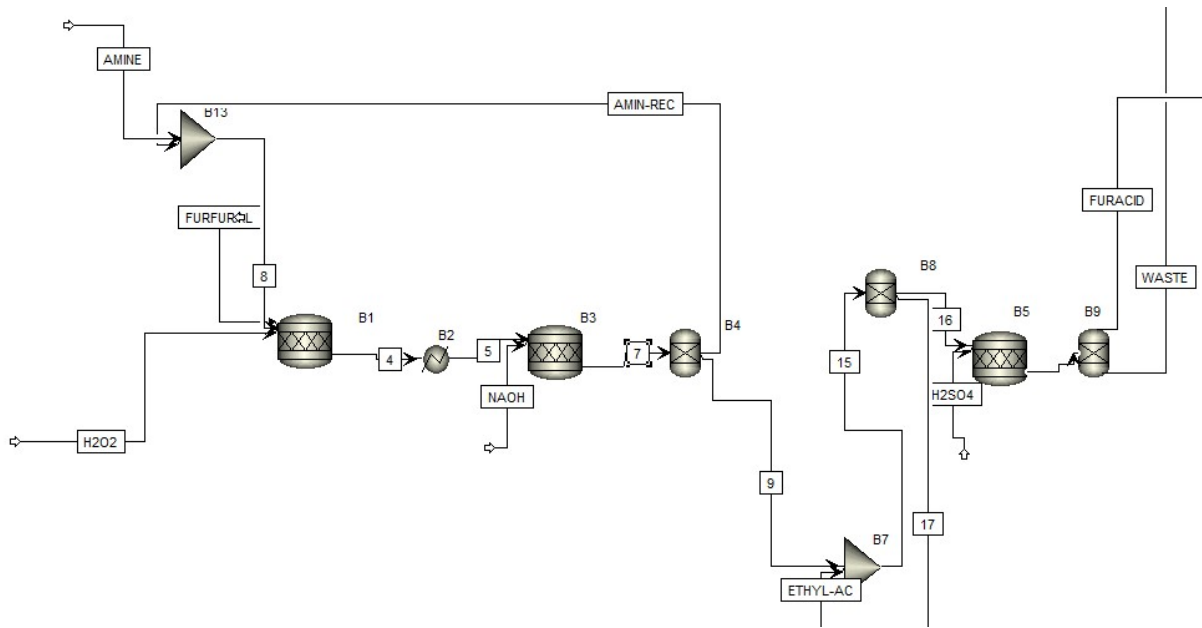


Figure S 4 Oxidation section of the furoic acid production

Esterification

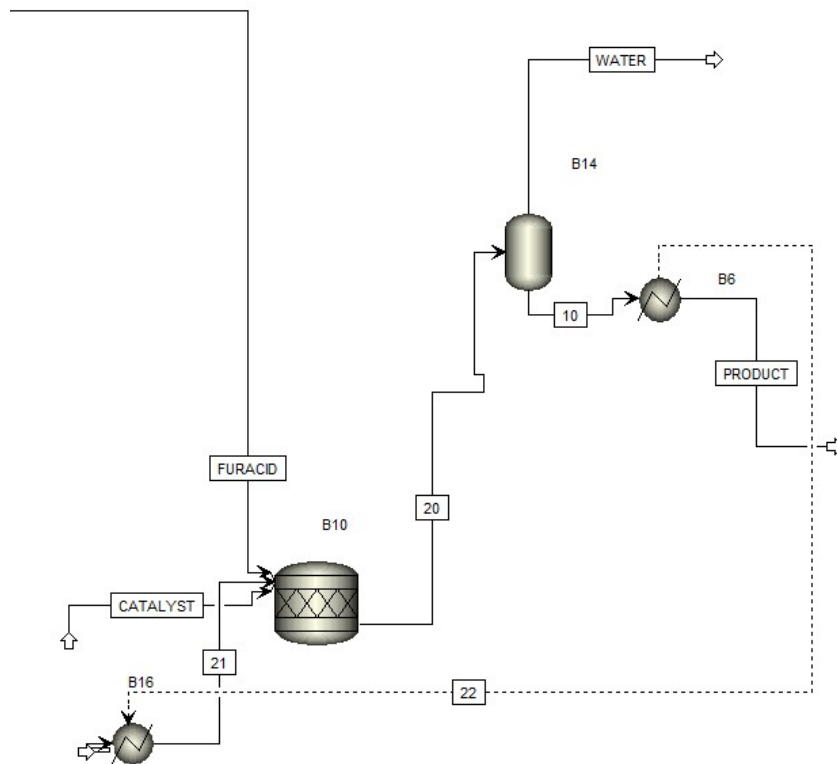


Figure S 5 Esterification section of to produce alkyl furoate from furoic acid and dodecanol

Amine oxide recovery

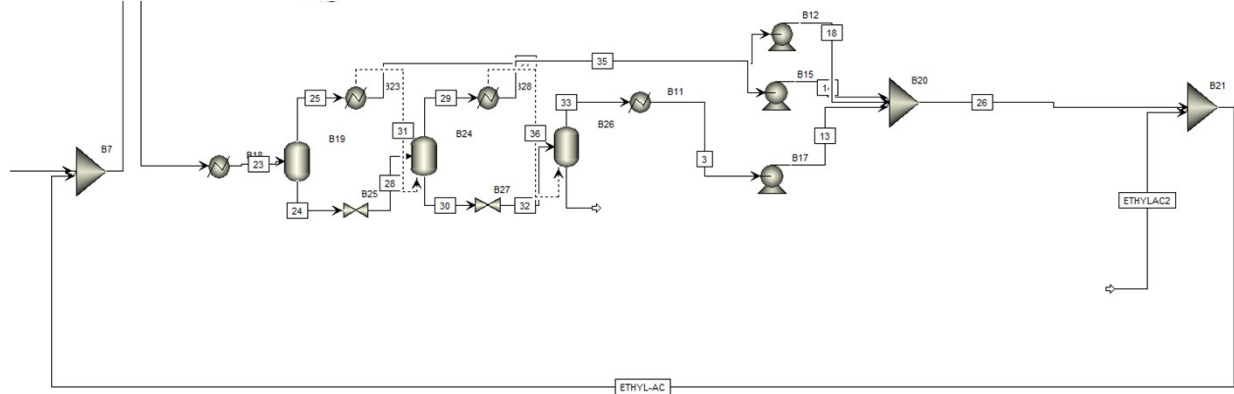


Figure S 6 Amine oxide recovery through multiple effect evaporator to remove ethyl acetate. Final ethyl acetate concentration 39 %. Nitrogen assisted evaporation not included in the simulation.

Sodium sulphate recovery

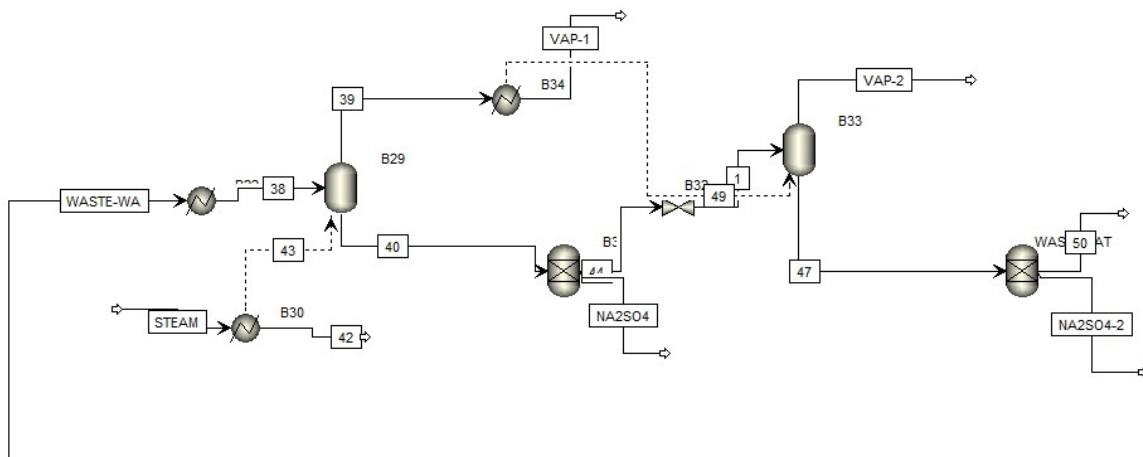


Figure S 7 Sodium sulphate recovery section with multiple effect evaporators

Results

Table S 5 Results of the economic parameter of the plant

Section	Productivity (Kg/h)	Annualized installed cost (k\$/year)	Operating costs (feedstock and utility, k\$/Kg)	Other operating costs k\$/Kg	Minimum selling price (\$/Kg)
Oxidation and work up section	1559	300	22,942	2,193	2,06
Esterification	3046	57	57,750	1,143	2.44
Amine Oxide	314	130	4,080	1,230	2.19
Sodium sulphate	738.7	154	1,770	1,366	0.56

Table S 6 Heating requirements of each section of the plant

Section	Energy requirements (MJ/h)	Steam required (Kg/h)
Oxidation	0	0
Esterification	2,817	1375
Amine Oxide	617	301
Sodium sulphate	4,001	1856

Capital cost estimation

Table S 7 Capital cost estimation expressed in k\$/year

Direct field cost	6,396
Direct field labour cost	1,599
Indirect field cost	1,839
Total field cost	9,834
Home office cost	1,919
Other project cost	1,955
Total project cost	23,542

Characterization

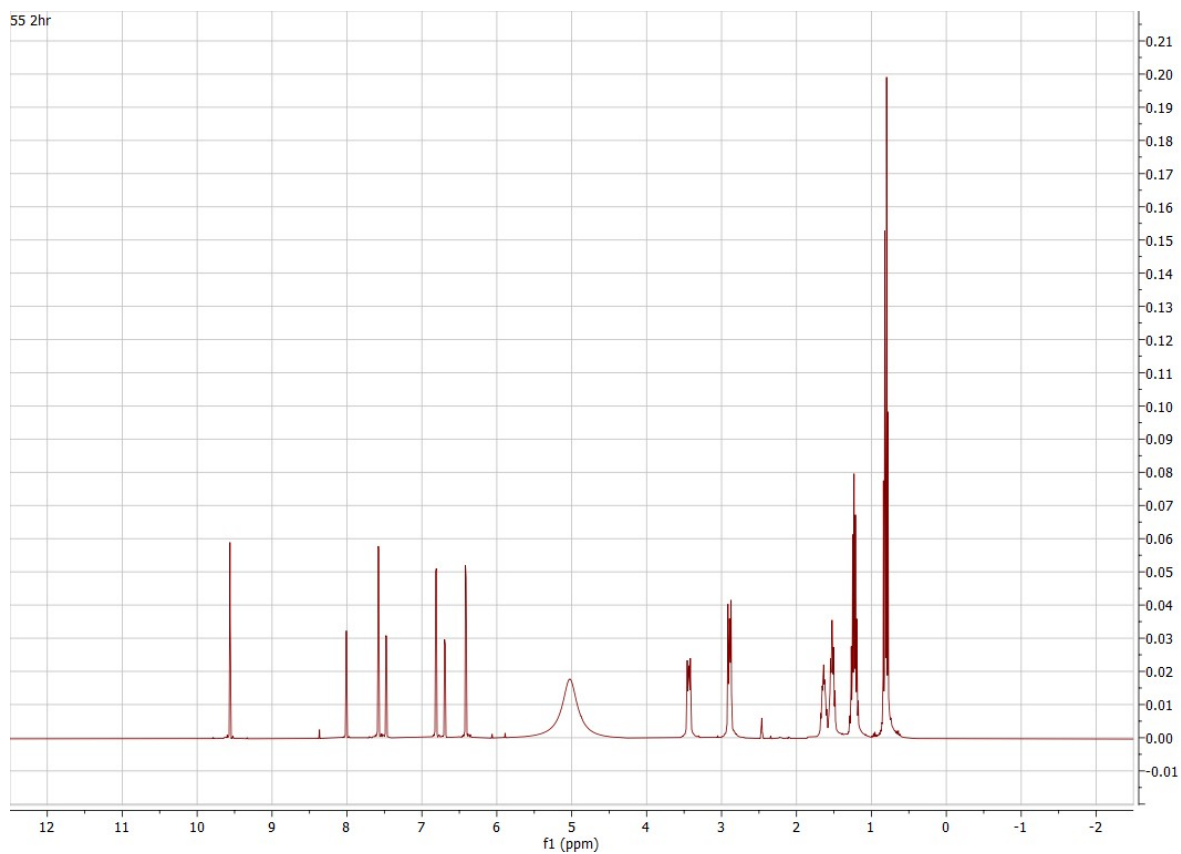


Figure S 8 Typical NMR of a reaction mixture in DMSO. 9.56 aldehyde signal of furfural, 7.6 , 6.8 ,6.36 furan ring of furfural. 8,7.46,6.7 furan ring furoic acid. Triplet 3.44 3*CH2 amine oxide, triplet 2.88 3*CH2 tributyl amine. Multiplete 1.63 3*CH2 tributyl amine oxide, multiplate 1.52 3*CH2 tributyl amine.

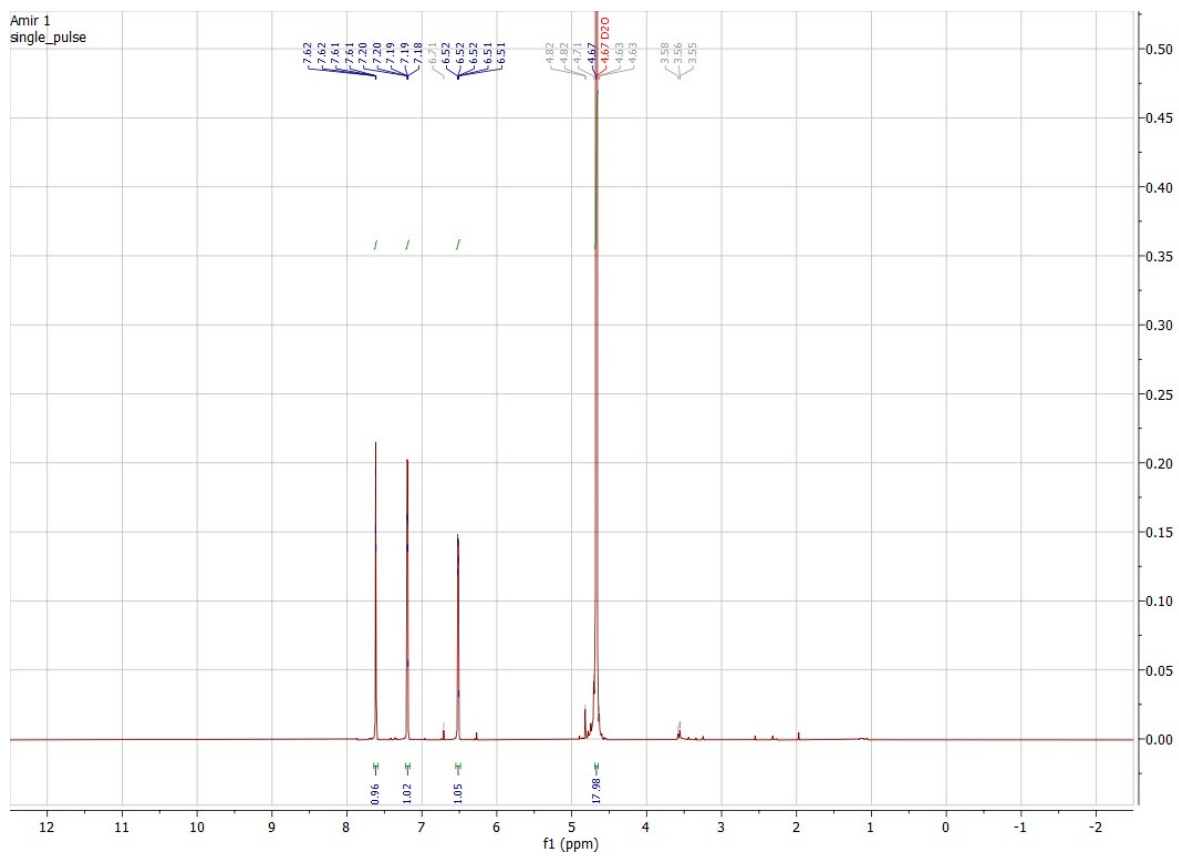


Figure S 9 Isolated furoic acid H-NMR spectra in D2O

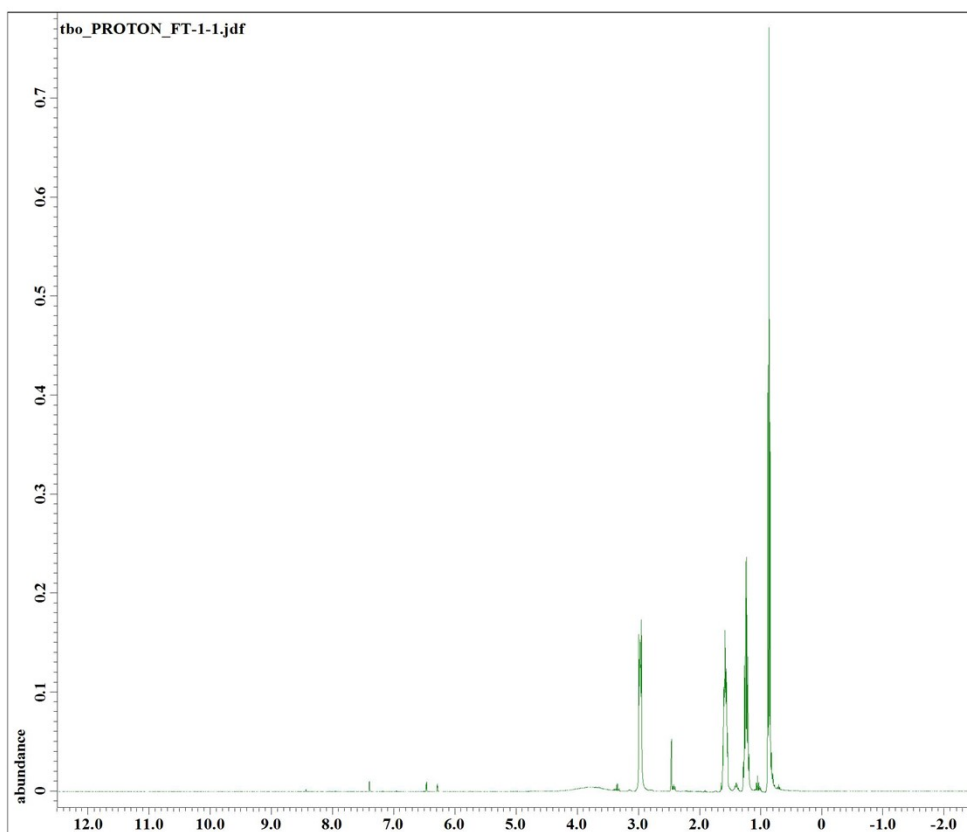


Figure S 10 Tributyl amine oxide H-NMR in DMSO

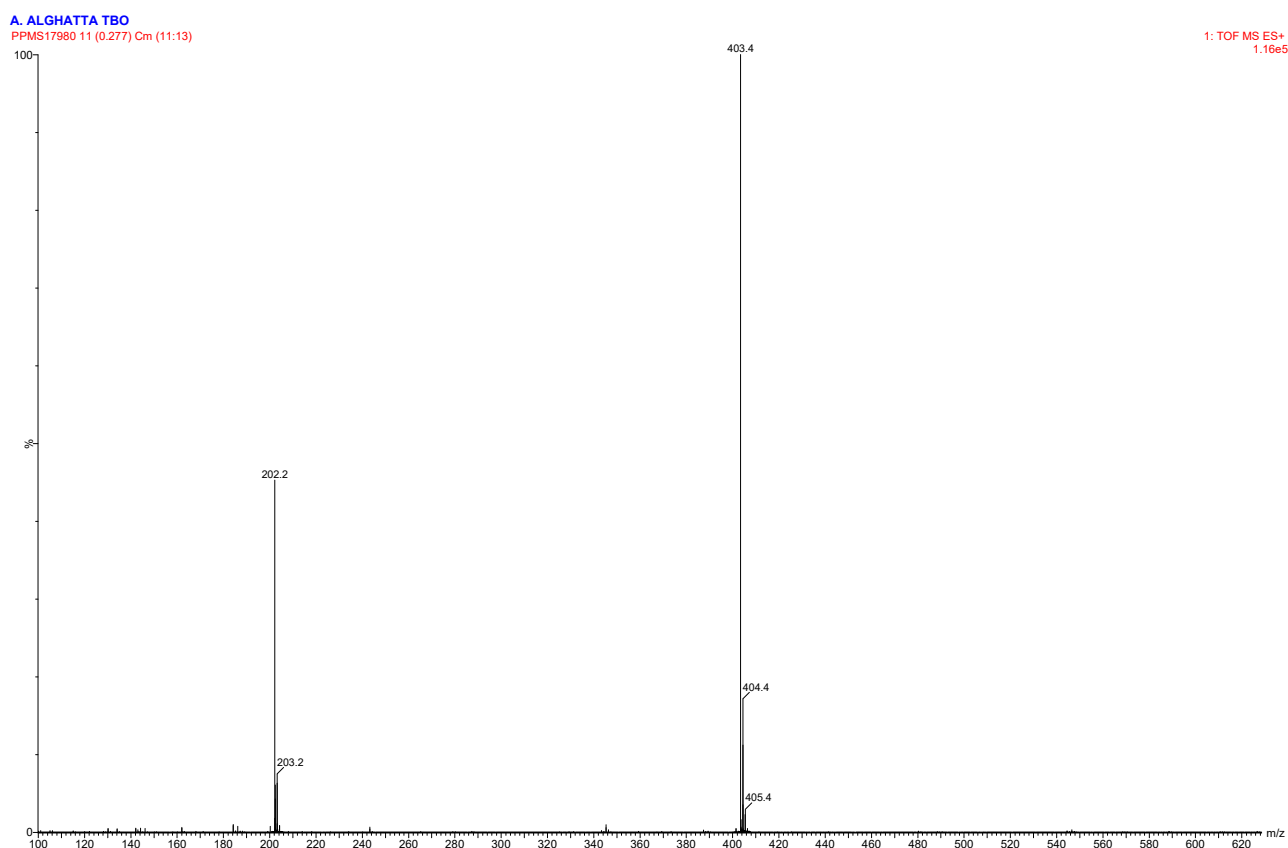


Figure S 11 Mass spectroscopy of the isolated tributyl amine oxide. 202.2 is referred to $[C_{12}H_{27}NOH]^+$ and 403.4 to the dimer $[C_{24}H_{34}N_2O_2H]^+$

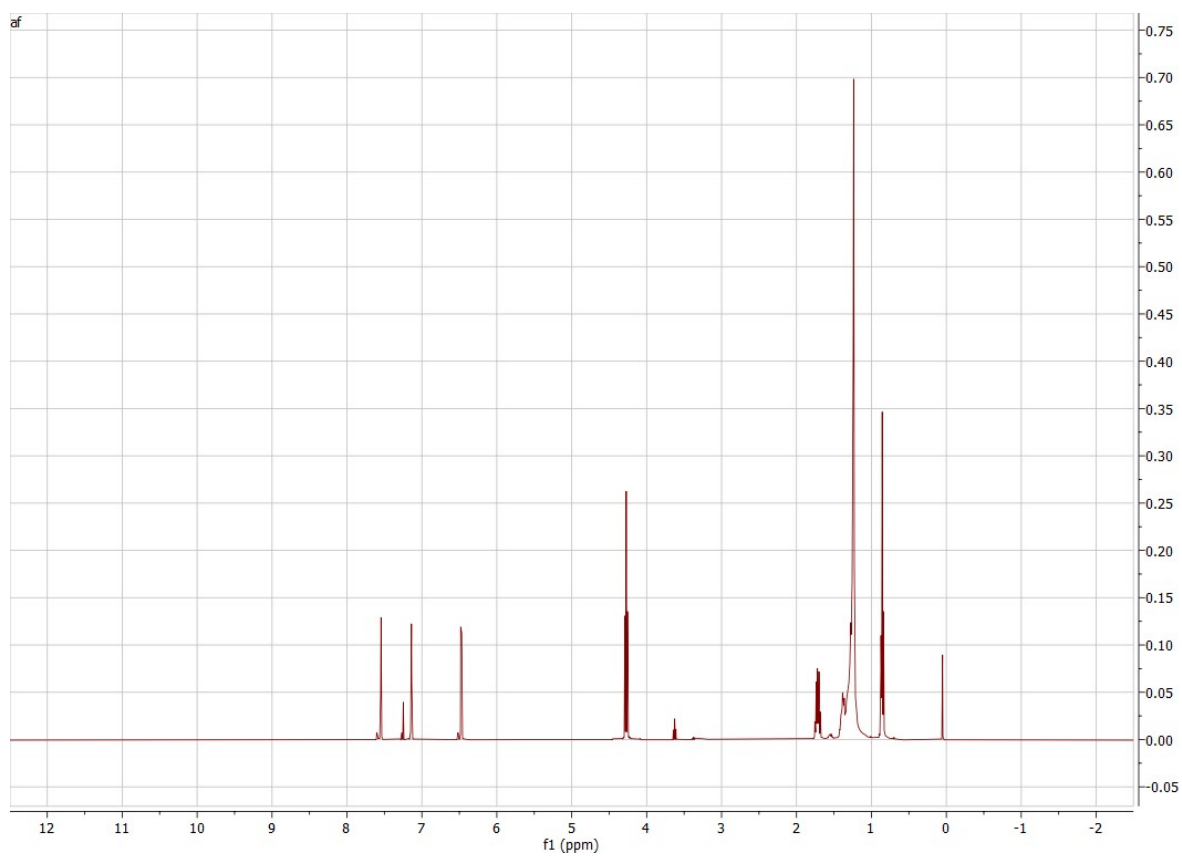


Figure S 12 H-NMR of the dodecyl furoate obtained from the esterification of the furoic acid and dodecanol

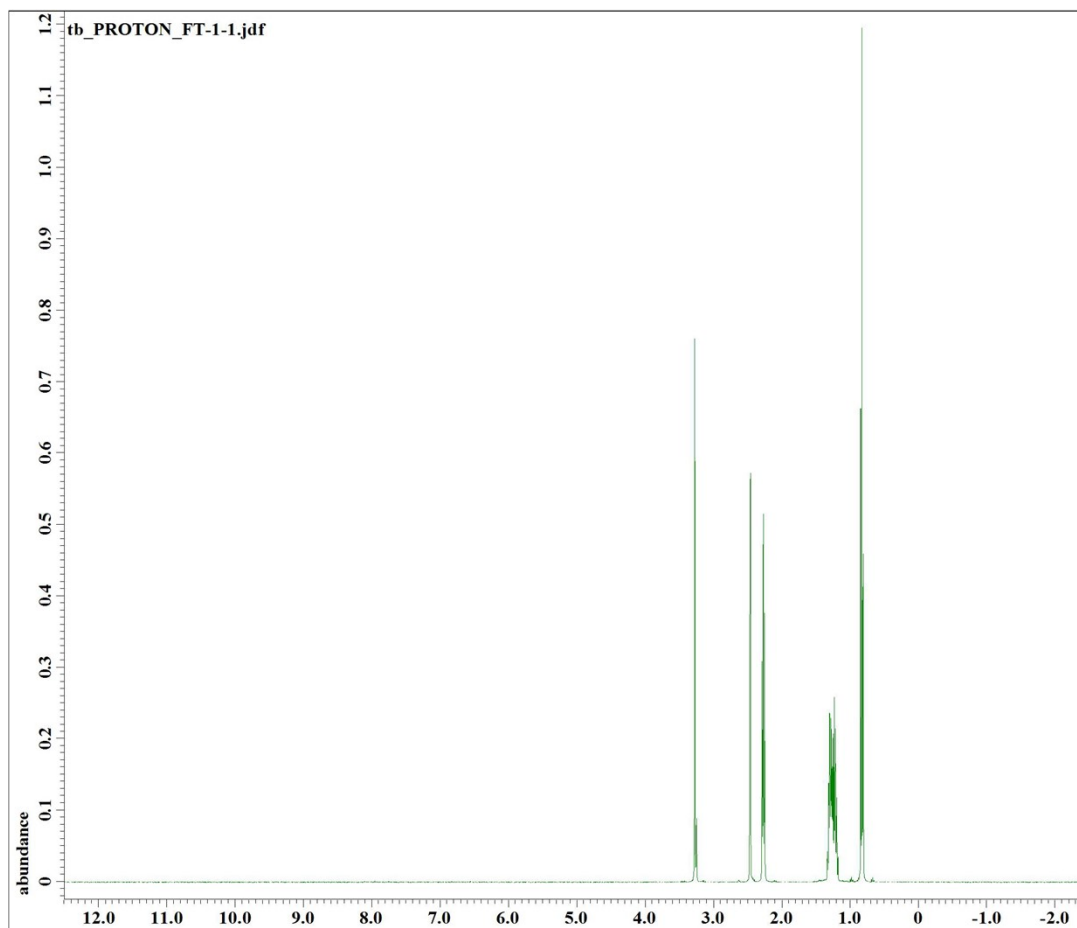


Figure S 13 H-NMR recovered tributyl amine after basification of the reaction mixture