Supporting Information

Stabilization of Polylactic Acid and Polyethylene with Nutshell Extract: Efficiency Assessment and Economic Evaluation

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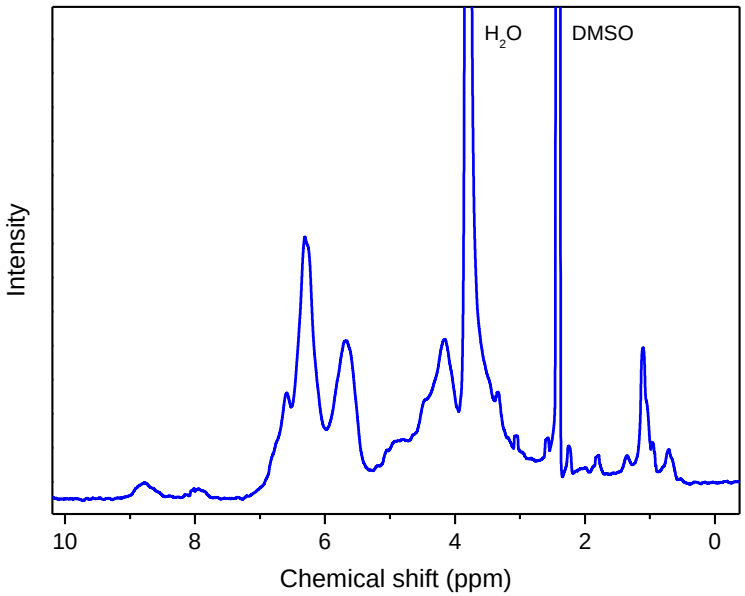
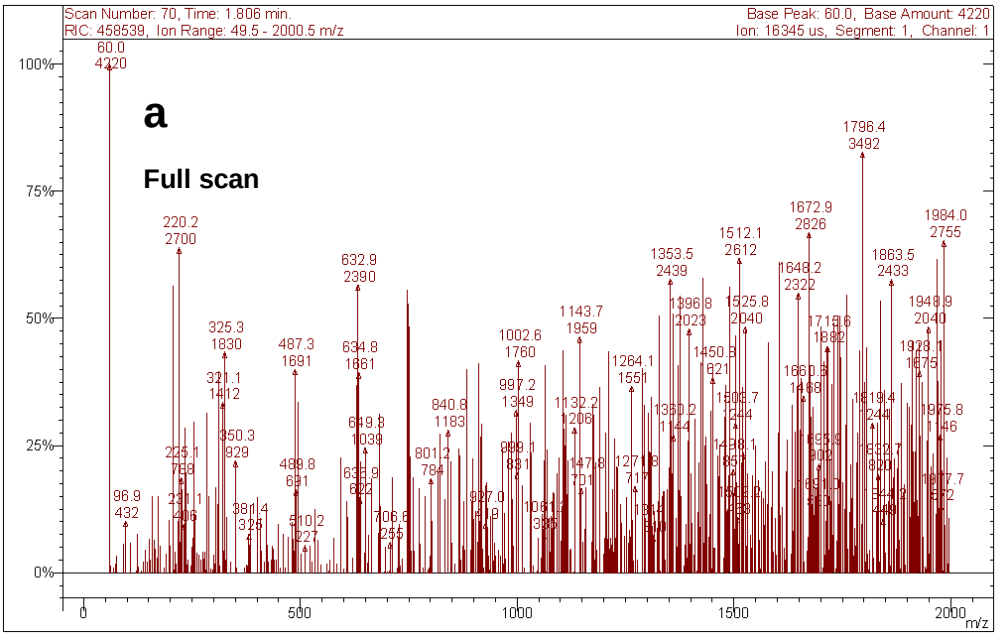
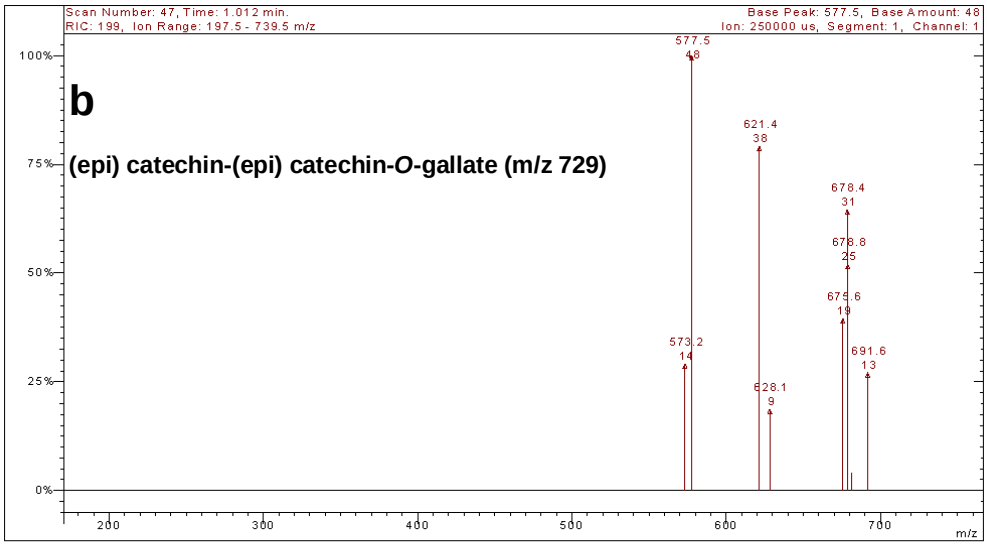


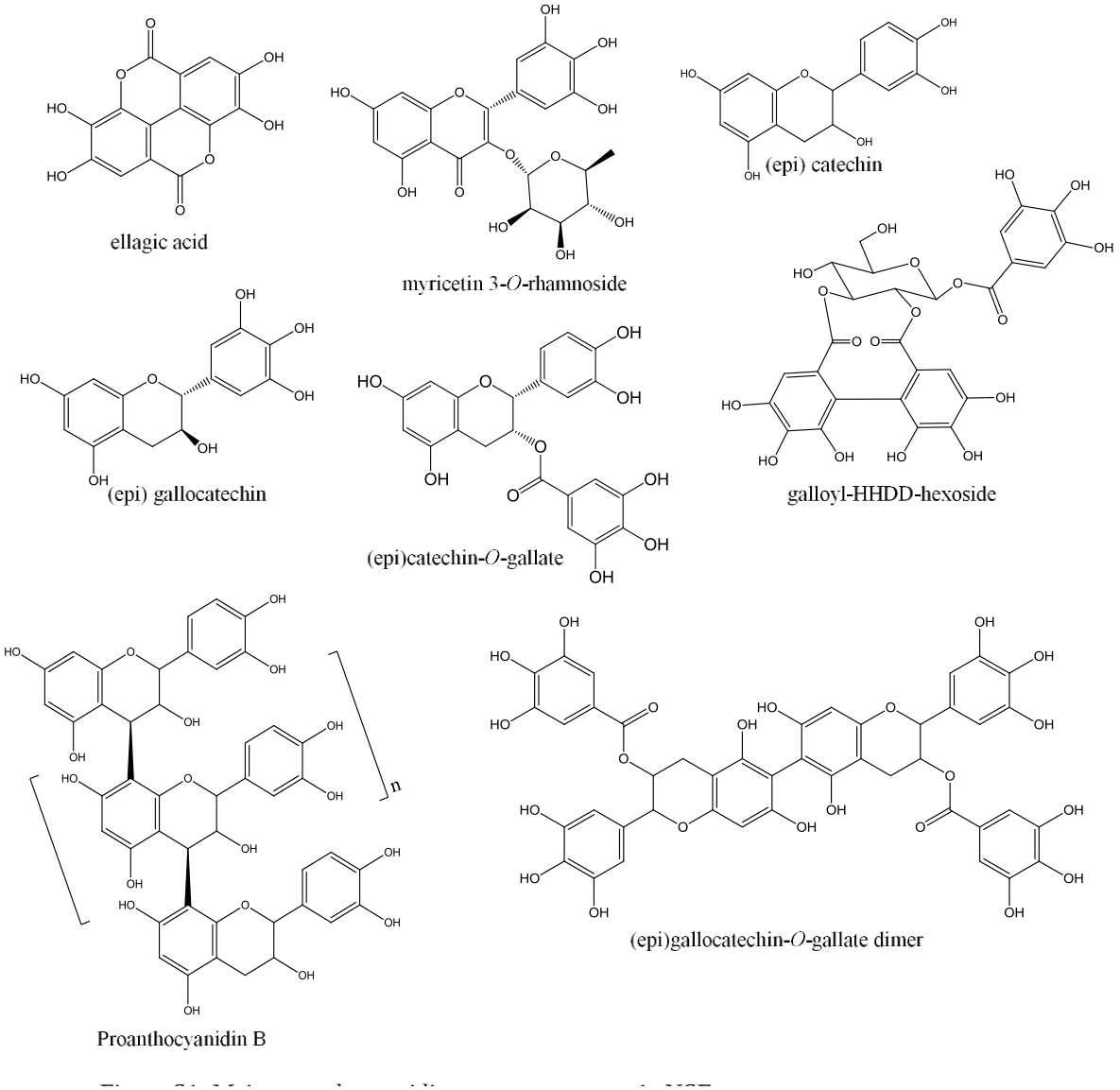
Figure S1. NMR spectrum of NSE in DMSO-d_6 after the addition of a few drops of D_2O to the sample.





Ion	Int Norm	Ion	Int Norm	Ion	Int Norm
573.2	14 291	628.1	9 187	678.8	25 520
577.5	48 999	675.6	19 395	681.5	2 42
621.4	38 791	678.4	31 645	691.6	13 271

Figure S2. FIA-ESI-IT-MS spectra of NSE: (a) full scan from 100 to 2000 m/z, and (b) MS/MS spectrum of the peak at 729 m/z (epi) catechin-(epi) catechin-*O*-gallate.



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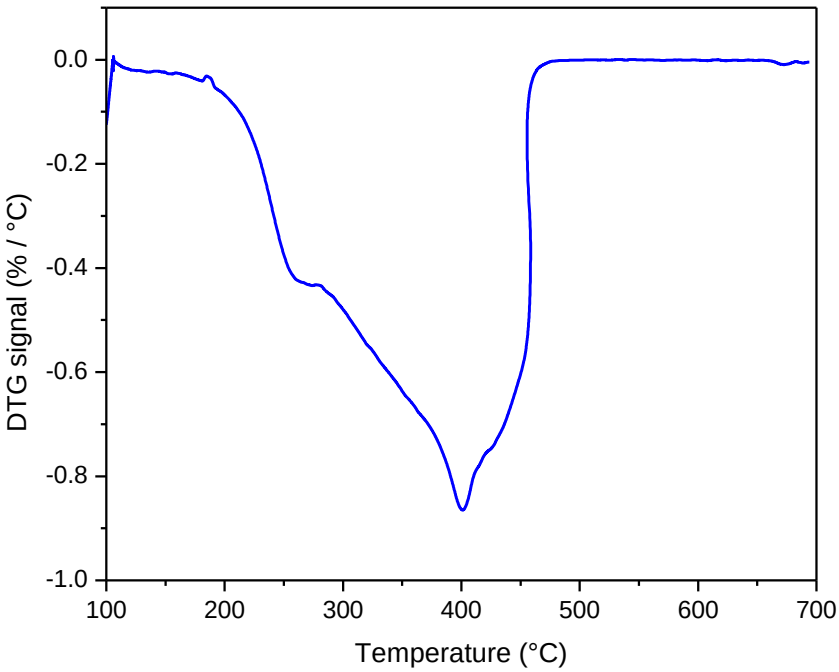


Figure S4. DTA curve of NSE under air atmosphere.

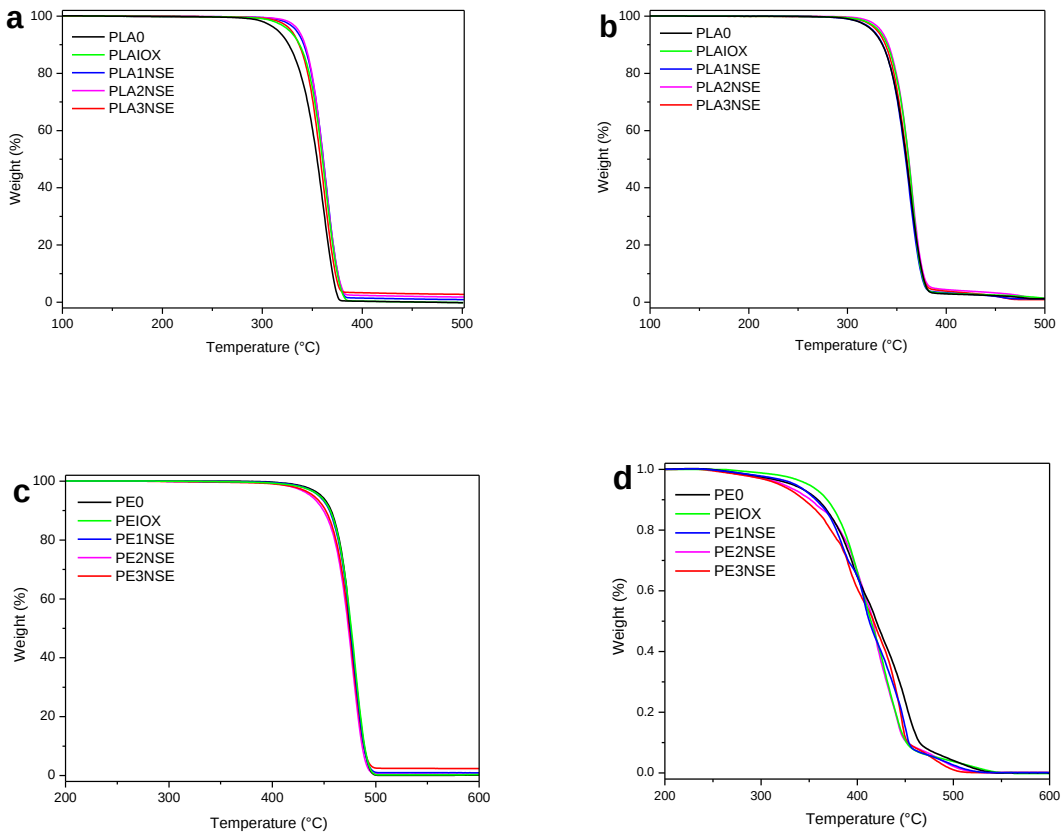


Figure S5. TG curves of neat and NSE-doped polymer films: (a) PLA under nitrogen, (b) PLA in air, (c) PE under nitrogen, (d) PE in air.

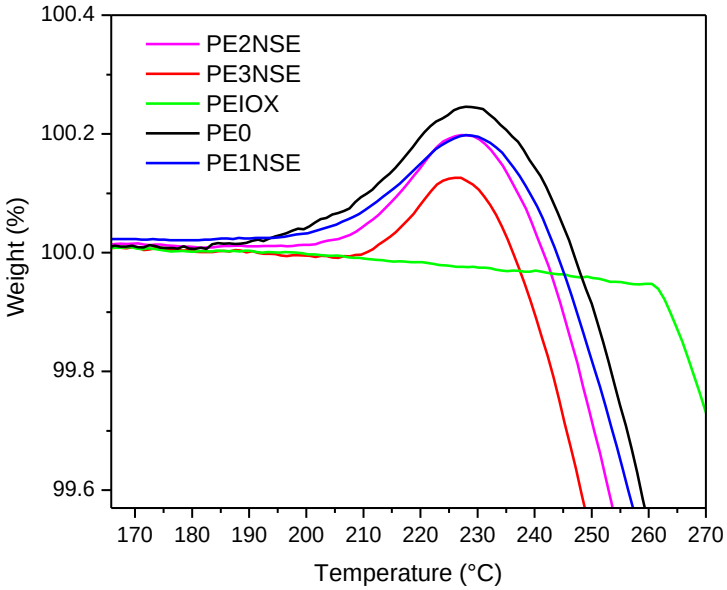


Figure S6. Detail of the TG curves in air of neat and NSE-doped PE films showing the weight gain due to oxygen chemisorption.

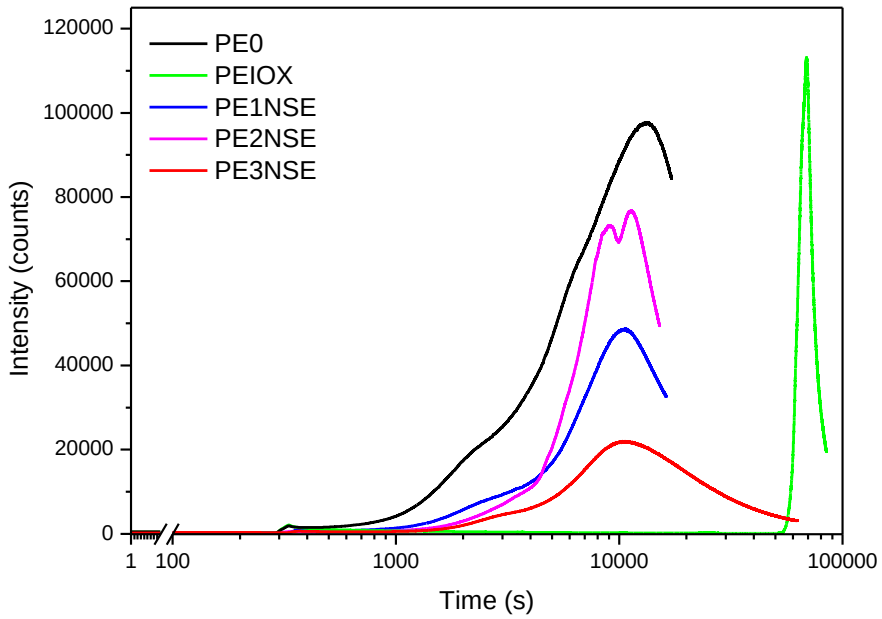
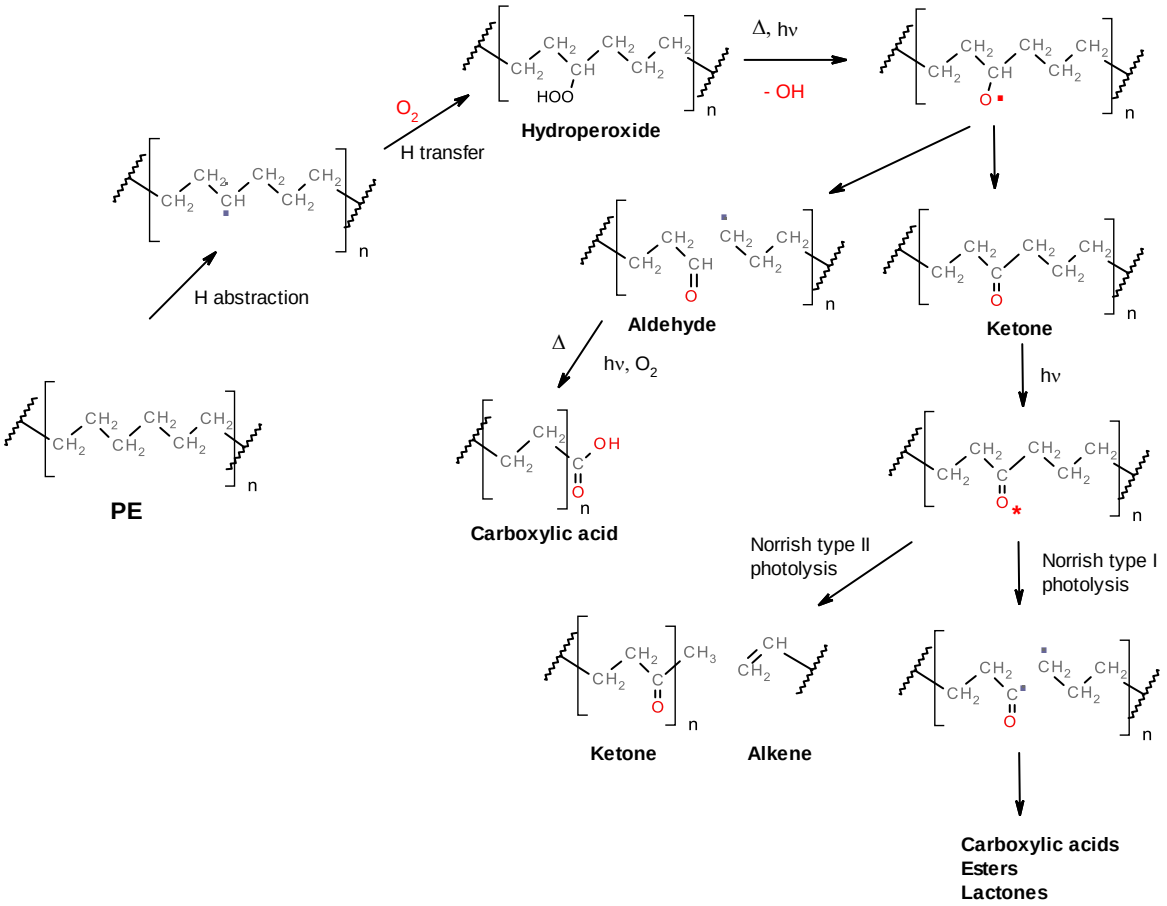
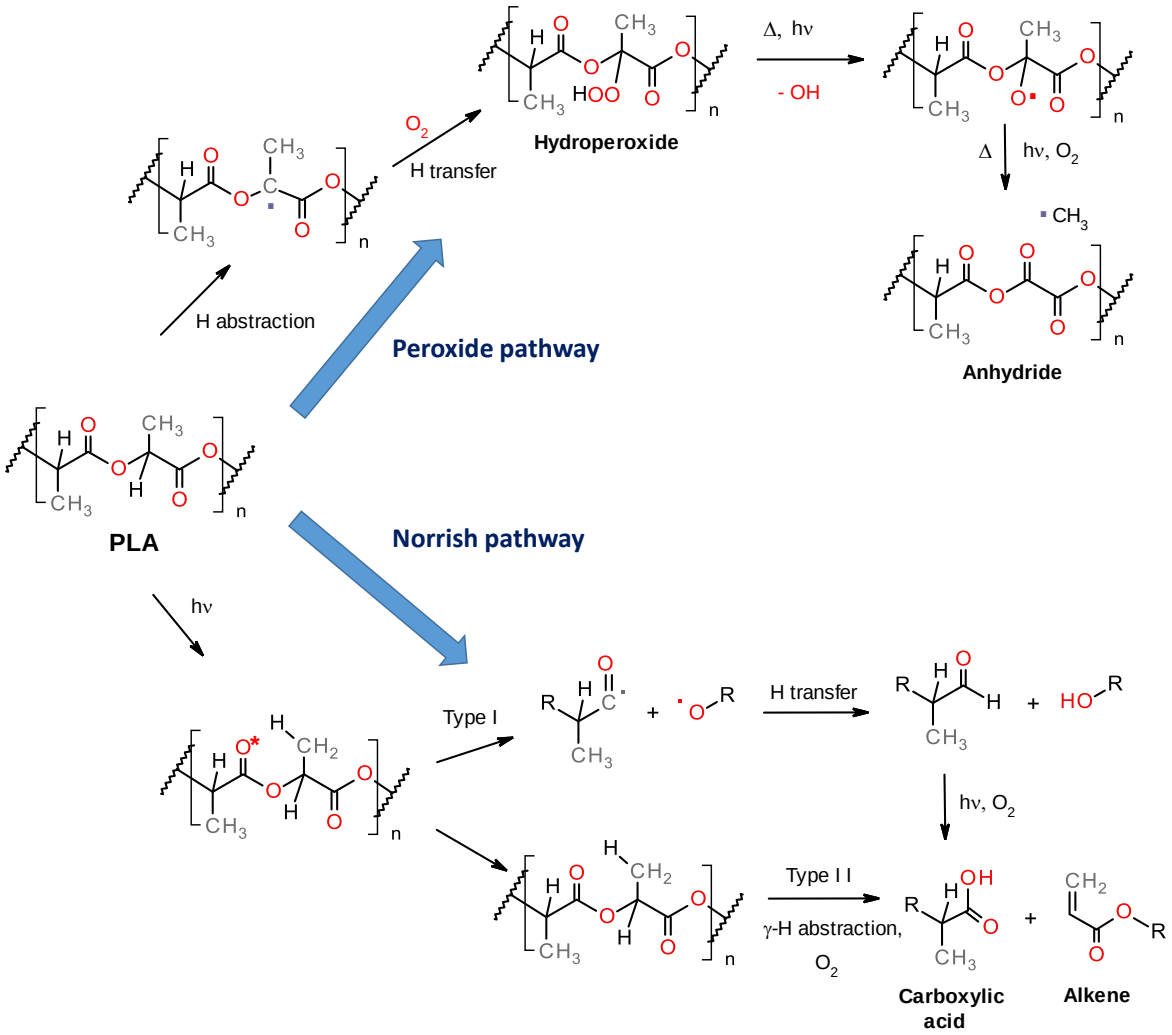


Figure S7. Isothermal runs of CL emission for neat and NSE-doped PE films under air.



Scheme S1. Simplified mechanism of thermal and photo-oxidation of polyethylene.



Scheme S2. Simplified mechanism of thermal and photo-oxidation of polylactic acid.

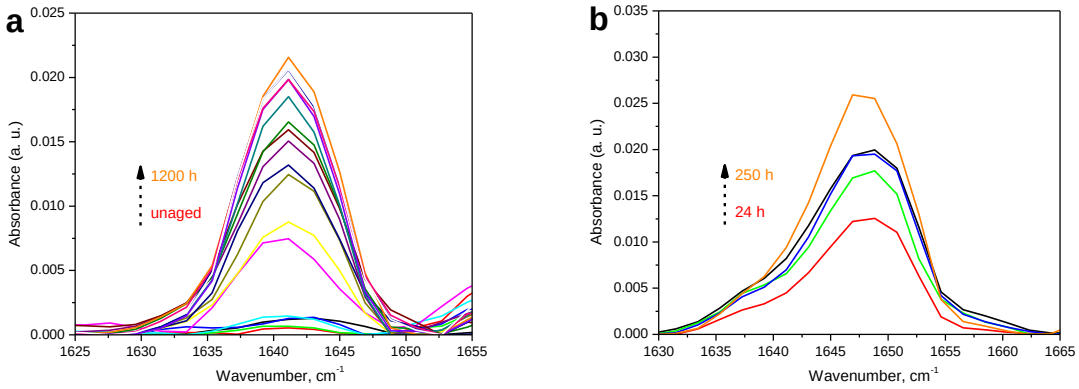


Figure S8. Evolution of the carbon-carbon double bond stretching peak in FTIR spectra of (a) PE0, and (b) PLA0 upon photo-irradiation.

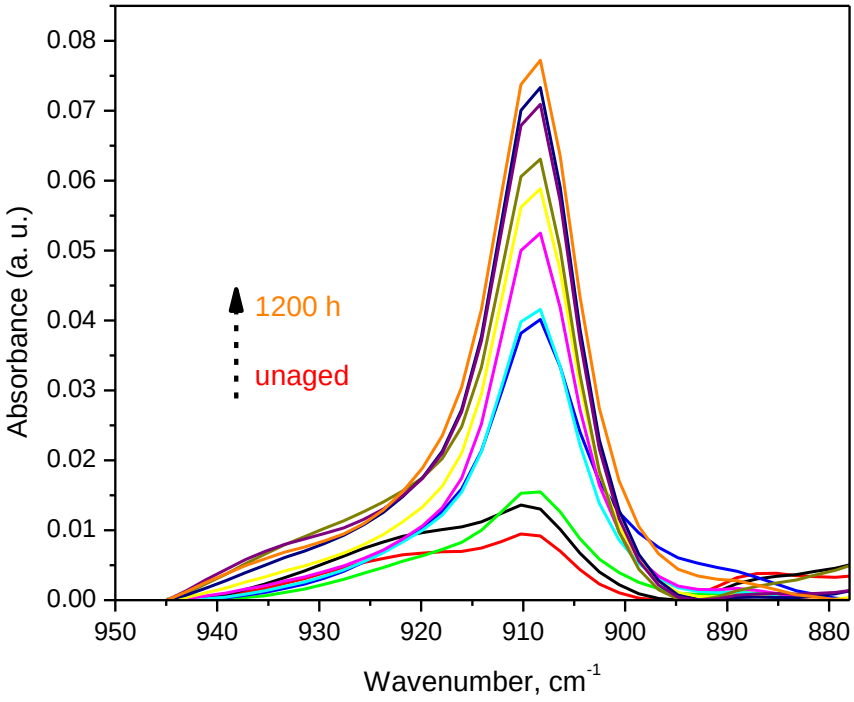


Figure S9. Evolution of the vinyl peak absorption in the FTIR spectra of photo-oxidized PE0.

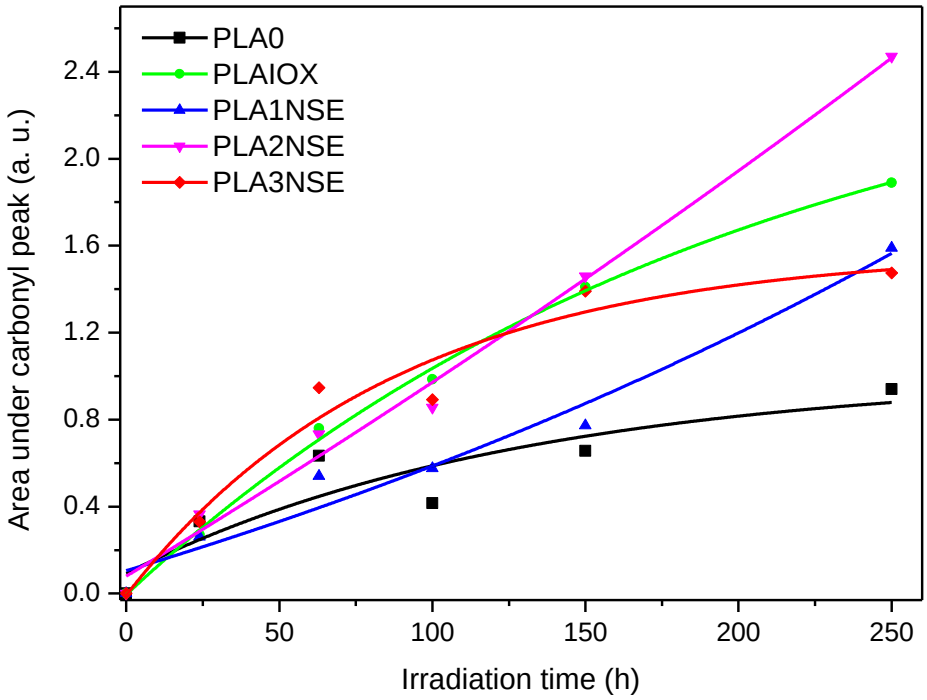


Figure S10. Increase of carboxylic acid groups (integration in the range between 1700 and 1720 cm^{-1}) in FTIR spectra of photo-oxidized PLA.

Table S1. Mechanical properties of unaged PLA and PE films*.

	Modulus (MPa)	Stress at break (MPa)	Strain at break (%)
PLA0	2582,7±83,2[b]	43,1±3,7[b]	19,6±5,1[b,c]
PLAIOX	2827,8±278,8[b,c]	43,3±4,9[b]	19,6±2,6[c]
PLA1NSE	2758,7±96,9[c]	43,8±3,9[b]	29,6±7,8[c]
PLA2NSE	2183,6±83,4[a]	36,7±0,8[a]	13,0±1,2[a]
PLA3NSE	2162,1±98,3[a]	33,1±3,1[a]	14,3±2,3[ab]
PE0	142,0±4,1[c]	23,7±1,0[c]	680,6±31,8[b]
PEIOX	69,1±10,4[a]	17,9±1,9[a,b]	650,8±54,6[b]
PE1NSE	103,0±4,1[b]	25,2±2,0[c]	681,2±32,3[b]
PE2NSE	74,0±8,0[a]	15,6±1,4[a]	531,7±29,7[a]
PE3NSE	91,1±8,1[b]	19,9±1,9[b]	640,1±16,4[b]

Average of ten determinations ± standard deviation. *Values in the same column (for same matrix), followed by the same letter indicates that there is no significant difference ($p > 0.05$).

Economic analysis input data

Raw materials costs

- Nutshell (NS): 0.06 USD/kg (http://www.quiminet.com/productos/cascara-de-nuez-molida-36113310873/precios.htm)
- Ethanol: 0.6 USD/L (http://www.bionavi.com.mx/)
- Distilled water: 0.54 USD/L (http://www.vadequimica.com/agua-destilada-25-60litros.html)

Energy cost

Electricity cost: 0.067 USD/kW-h
(http://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_5_03)

Equipment operating cost

Operating times and electricity consumption of the batch process were calculated based on the technical specifications of the following equipment:

- Ultrasonic Branson 8510 (http://muquip.triumf.ca/sites/default/files//instruction_manuals/mnl_ultrasonic_cleaner_1_0.pdf)
- Centrífugas Decanter Flottweg (https://www.flottweg.com/es/la-gama-de-productos/centrifugas/)
- 50L Big Volume Lab Rotary Evaporators RE5002 (http://www.kdinstrument.com/products/50L_Big_Volume_Lab_Rotary_Evaporators.html#S3)

Table S2. Estimated costs of manufacturing 1 kg of NSE in a batch process.

Raw material cost			
	Unit cost (USD kg^{-1})	Amount (kg)	Cost (USD)
Nutshell powdered	0.06	6.92	0.41
Ethanol	0.6	32.7	19.62
Distilled water	0.054	27.6	1.49
Cooling water	0.00034	50	0.017
Total			**21.53**
Energy consumption cost			
	Power use (kW h^{-1})	Time of operation (h)	Cost (USD)
Ultrasound extraction	0.32	1	0.021
Solid-liquid separation	1.5	0.5	0.050
Solvent evaporation	10.2	4.5	3.089
Total			**3.16**
NSE cost per kg			**24.69**

Table S3. Economic parameters used in the process simulation to estimate NSE manufacturing cost in the continuous process.

Description	Cost (USD)
Equipment Costs	
3 Extraction tanks	849 000
3 Centrifugal pumps	33 000
Decanter tank	37 000
Thin film evaporator	107 000
Spray dryer	116 000
Condenser	39 000
Heat exchanger	9 000
Unlisted equipment	298 000
Raw Materials Cost	
Ethyl alcohol (L^{-1})	0.60
Ground NS (Kg^{-1})	0.60
Water (L^{-1})	0.054
Labor Cost	
Operator Unit cost (h^{-1})	14.90
Number of operators	9
Utilities Cost	
Electricity (kW^{-1})	0.067
Steam (MT)	12.00
Chilled water (MT)	0.40

NSE 1:10 Economic Evaluation Report

March 24, 2017

1. EXECUTIVE SUMMARY (2017 prices)

Total Capital Investment	9,004,000 $
Capital Investment Charged to This Project	9,004,000 $
Operating Cost	1,887,000 $/yr
Net Operating Cost	1,887,085 $/yr
Revenues	1,071,000 $/yr
Cost Basis Annual Rate	53,552 kg MP/yr
Unit Production Cost	35.24 $/kg MP
Net Unit Production Cost	35.24 $/kg MP
Unit Production Revenue	20.00 $/kg MP
Gross Margin	- 76.19 %
Return On Investment	- 0.04 %
Payback Time	N/A
IRR (After Taxes)	N/A
NPV (at 7.0% Interest)	- 8,605,000 $

MP = Flow of Component 'NSE' in Stream 'S-108'

2. MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2017 prices)

Quantity/ Standby/ Staggered	Name	Description	Unit Cost ($)	Cost ($)
3 / 0 / 0	V-101	Blending Tank	283,000	849,000
		Vessel Volume = 6000.00 L		
1 / 0 / 0	V-103	Decanter Tank	37,000	37,000
		Vessel Volume = 26.02 L		
1 / 0 / 0	TFE-101	Thin Film Evaporator	107,000	107,000
		Film Area = 0.12 m2		
1 / 0 / 0	SDR-101	Spray Dryer	116,000	116,000
		Dryer Volume = 205.89 L		
1 / 0 / 0	HX-101	Condenser	39,000	39,000
		Condensation Area = 1.11 m2		
1 / 0 / 0	PM-101	Centrifugal Pump	11,000	11,000
		Pump Power = 0.00 kW		
1 / 0 / 0	PM-102	Centrifugal Pump	11,000	11,000
		Pump Power = 0.01 kW		
1 / 0 / 0	PM-103	Centrifugal Pump	11,000	11,000
		Pump Power = 0.01 kW		
1 / 0 / 0	HX-102	Heat Exchanger	9,000	9,000
		Heat Exchange Area = 0.02 m2		
		Unlisted Equipment		298,000
			TOTAL	1,488,000

3. FIXED CAPITAL ESTIMATE SUMMARY (2017 prices in $)

3A. Total Plant Direct Cost (TPDC) (physical cost)	
1. Equipment Purchase Cost	1,488,000
2. Installation	361,000
3. Process Piping	521,000
4. Instrumentation	595,000
5. Insulation	45,000
6. Electrical	149,000
7. Buildings	669,000
8. Yard Improvement	223,000
9. Auxiliary Facilities	595,000
TPDC	4,645,000

3B. Total Plant Indirect Cost (TPIC)	
10. Engineering	1,161,000
11. Construction	1,626,000
TPIC	2,787,000

3C. Total Plant Cost (TPC = TPDC+TPIC)	
TPC	7,433,000

3D. Contractor's Fee & Contingency (CFC)	
12. Contractor's Fee	372,000
13. Contingency	743,000
CFC = 12+13	1,115,000

3E. Direct Fixed Capital Cost (DFC = TPC+CFC)	
DFC	8,547,000

4. LABOR COST - PROCESS SUMMARY

Labor Type	Unit Cost ($/h)	Annual Amount (h)	Annual Cost ($)	%
Operator	14.90	16,467	245,417	100.00
TOTAL		16,467	245,417	100.00

5. MATERIALS COST - PROCESS SUMMARY

Bulk Material	Unit Cost ($)	Annual Amount		Annual Cost ($)	%
Ethyl Alcohol	0.600	28,752	L(STP)	17,251	35.64
NS	0.060	357,014	kg	21,421	44.25
Water	0.054	179,601	L(STP)	9,735	20.11
Air	0.000	815,305	kg	0	0.00
TOTAL				48,408	100.00

NOTE: Bulk material consumption amount includes material used as:
- Raw Material
- Cleaning Agent
- Heat Transfer Agent (if utilities are included in the operating cost)

8. UTILITIES COST (2017 prices) - PROCESS SUMMARY

Utility	Unit Cost ($)	Annual Amount	Ref. Units	Annual Cost ($)	%
Std Power	0.100	6,153	kW-h	615	2.34
High Voltage	20.603	150	kW-h	3,085	11.75
Steam	12.000	699	MT	8,385	31.93
Chilled Water	0.400	35,432	MT	14,173	53.97
TOTAL				26,258	100.00

9. ANNUAL OPERATING COST (2017 prices) - PROCESS SUMMARY

Cost Item	$	%
Raw Materials	48,000	2.57
Labor-Dependent	245,000	13.01
Facility-Dependent	1,567,000	83.04
Utilities	26,000	1.39
Advertising/Selling	0	0.00
Running Royalties	0	0.00
Failed Product Disposal	0	0.00
TOTAL	1,887,000	100.00

10. PROFITABILITY ANALYSIS (2017 prices)

A.	Direct Fixed Capital	8,547,000 $
B.	Working Capital	29,000 $
C.	Startup Cost	427,000 $
D.	Up-Front R&D	0 $
E.	Up-Front Royalties	0 $
F.	Total Investment (A+B+C+D+E)	9,004,000 $
G.	Investment Charged to This Project	9,004,000 $
H.	**Revenue/Savings Rates**	
	S-108 (Main Revenue)	61,815 kg /yr
I.	**Revenue/Savings Price**	
	S-108 (Main Revenue)	17.33 $/kg
J.	**Revenues/Savings**	
	S-108 (Main Revenue)	1,071,041 $/yr
1	Total Revenues	1,071,041 $/yr
2	Total Savings	0 $/yr
K.	**Annual Operating Cost (AOC)**	
1	Actual AOC	1,887,000 $/yr
2	Net AOC (K1-J2)	1,887,000 $/yr
L.	**Unit Production Cost /Revenue**	
	Unit Production Cost	35.24 $/kg MP
	Net Unit Production Cost	35.24 $/kg MP
	Unit Production Revenue	20.00 $/kg MP
M.	Gross Profit (J-K)	- 817,000 $/yr
N.	Taxes (40%)	0 $/yr
O.	Net Profit (M-N + Depreciation)	- 5,000 $/yr
	Gross Margin	- 76.19 %
	Return On Investment	- 0.04 %
	Payback Time	N/A

MP = Flow of Component 'NSE' in Stream 'S-108'

NSE 1:4 Economic Evaluation Report

March 24, 2017

1. EXECUTIVE SUMMARY (2017 prices)

Total Capital Investment	9,008,000 $
Capital Investment Charged to This Project	9,008,000 $
Operating Cost	1,935,000 $/yr
Net Operating Cost	1,934,889 $/yr
Revenues	2,687,000 $/yr
Cost Basis Annual Rate	134,336 kg MP/yr
Unit Production Cost	14.40 $/kg MP
Net Unit Production Cost	14.40 $/kg MP
Unit Production Revenue	20.00 $/kg MP
Gross Margin	27.98 %
Return On Investment	14.02 %
Payback Time	7.13 years
IRR (After Taxes)	6.95 %
NPV (at 7.0% Interest)	- 4,000 $

MP = Flow of Component 'NSE' in Stream 'S-108'

2. MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2017 prices)

Quantity/ Standby/ Staggered	Name	Description	Unit Cost ($)	Cost ($)
3 / 0 / 0	V-101	Blending Tank	283,000	849,000
		Vessel Volume = 6000.00 L		
1 / 0 / 0	V-103	Decanter Tank	37,000	37,000
		Vessel Volume = 24.97 L		
1 / 0 / 0	TFE-101	Thin Film Evaporator	107,000	107,000
		Film Area = 0.12 m2		
1 / 0 / 0	SDR-101	Spray Dryer	116,000	116,000
		Dryer Volume = 205.88 L		
1 / 0 / 0	HX-101	Condenser	39,000	39,000
		Condensation Area = 1.11 m2		
1 / 0 / 0	PM-101	Centrifugal Pump	11,000	11,000
		Pump Power = 0.00 kW		
1 / 0 / 0	PM-102	Centrifugal Pump	11,000	11,000
		Pump Power = 0.01 kW		
1 / 0 / 0	PM-103	Centrifugal Pump	11,000	11,000
		Pump Power = 0.01 kW		
1 / 0 / 0	HX-102	Heat Exchanger	9,000	9,000
		Heat Exchange Area = 0.02 m2		
		Unlisted Equipment		298,000
			TOTAL	1,488,000

3. FIXED CAPITAL ESTIMATE SUMMARY (2017 prices in $)

3A. Total Plant Direct Cost (TPDC) (physical cost)	
1. Equipment Purchase Cost	1,488,000
2. Installation	361,000
3. Process Piping	521,000
4. Instrumentation	595,000
5. Insulation	45,000
6. Electrical	149,000
7. Buildings	669,000
8. Yard Improvement	223,000
9. Auxiliary Facilities	595,000
TPDC	4,645,000

3B. Total Plant Indirect Cost (TPIC)	
10. Engineering	1,161,000
11. Construction	1,626,000
TPIC	2,787,000

3C. Total Plant Cost (TPC = TPDC+TPIC)	
TPC	7,433,000

3D. Contractor's Fee & Contingency (CFC)	
12. Contractor's Fee	372,000
13. Contingency	743,000
CFC = 12+13	1,115,000

3E. Direct Fixed Capital Cost (DFC = TPC+CFC)	
DFC	8,547,000

4. LABOR COST - PROCESS SUMMARY

Labor Type	Unit Cost ($/h)	Annual Amount (h)	Annual Cost ($)	%
Operator	14.90	17,461	260,241	100.00
TOTAL		17,461	260,241	100.00

5. MATERIALS COST - PROCESS SUMMARY

Bulk Material	Unit Cost ($)	Annual Amount		Annual Cost ($)	%
Ethyl Alcohol	0.600	28,752	L(STP)	17,251	21.37
NS	0.060	895,574	kg	53,734	66.57
Water	0.054	179,601	L(STP)	9,735	12.06
Air	0.000	815,268	kg	0	0.00
TOTAL				80,721	100.00

NOTE: Bulk material consumption amount includes material used as:
- Raw Material
- Cleaning Agent
- Heat Transfer Agent (if utilities are included in the operating cost)

8. UTILITIES COST (2017 prices) - PROCESS SUMMARY

Utility	Unit Cost ($)	Annual Amount	Ref. Units	Annual Cost ($)	%
Std Power	0.100	8,239	kW-h	824	3.06
High Voltage	20.603	161	kW-h	3,307	12.28
Steam	12.000	719	MT	8,624	32.03
Chilled Water	0.400	35,419	MT	14,168	52.62
TOTAL				26,923	100.00

9. ANNUAL OPERATING COST (2017 prices) - PROCESS SUMMARY

Cost Item	$	%
Raw Materials	81,000	4.17
Labor-Dependent	260,000	13.45
Facility-Dependent	1,567,000	80.99
Utilities	27,000	1.39
Advertising/Selling	0	0.00
Running Royalties	0	0.00
Failed Product Disposal	0	0.00
TOTAL	1,935,000	100.00

10. PROFITABILITY ANALYSIS (2017 prices)

A.	Direct Fixed Capital	8,547,000 $
B.	Working Capital	33,000 $
C.	Startup Cost	427,000 $
D.	Up-Front R&D	0 $
E.	Up-Front Royalties	0 $
F.	Total Investment (A+B+C+D+E)	9,008,000 $
G.	Investment Charged to This Project	9,008,000 $
H.	**Revenue/Savings Rates**	
	S-108 (Main Revenue)	142,599 kg /yr
I.	**Revenue/Savings Price**	
	S-108 (Main Revenue)	18.84 $/kg
J.	**Revenues/Savings**	
	S-108 (Main Revenue)	2,686,721 $/yr
1	Total Revenues	2,686,721 $/yr
2	Total Savings	0 $/yr
K.	**Annual Operating Cost (AOC)**	
1	Actual AOC	1,935,000 $/yr
2	Net AOC (K1-J2)	1,935,000 $/yr
L.	**Unit Production Cost /Revenue**	
	Unit Production Cost	14.40 $/kg MP
	Net Unit Production Cost	14.40 $/kg MP
	Unit Production Revenue	20.00 $/kg MP
M.	Gross Profit (J-K)	752,000 $/yr
N.	Taxes (40%)	301,000 $/yr
O.	Net Profit (M-N + Depreciation)	1,263,000 $/yr
	Gross Margin	27.98 %
	Return On Investment	14.02 %
	Payback Time	7.13 years

MP = Flow of Component 'NSE' in Stream 'S-108'